United States Court of Appeals for the Second Circuit



APPENDIX

DEFERRED JOINT APPENDIX TO THE BRIEFS Vol. 3 of 3 Pages 1191 - 1800



IN THE

UNITED STATES COURT OF APPEALS
FOR THE SECOND CIRCUIT

No. 74-1683

74-1007

HOOKER CHEMICALS AND PLASTICS COPPOPATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

No. 74-1687

HOOKER CHEMICALS AND PLASTICS CORPORATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

On Petition For Review Of Action Of The Administrator Of The Environmental Projection Agency

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SECTION I SUMMARY

I. SCOPE

The purpose of this report is to assess the economic impact of the 1972 Federal Water Pollution Control Amendments on the industrial phosphate industry. The specific products analyzed are as follows:

- → Phosphorus
- -Phosphoric acid produced from phosphorus
- -Phosphorus pentoxide
- -Phosphorus trichloride
- Phosphorus oxychloride
- ~ Phosphorus pentasulfide
- -Sodium tripolyphosphate (STPP)
- ~ Calcium phosphates (excluding fertilizers, and defluorinated phosphates)

II. SEGMENTATION

The industry producing the products listed above was segmented for analysis on the basis of process similarity. This was considered a more valid basis than geographic location, age or size of plant, or other possible criteria.

The four segments selected were as follows:

- 1. Elemental phosphorus
- 2. Phosphoric acid
- 3. Anhydrous derivatives of phosphorus (phosphorus pentoxide, pentasulfide, trichloride, and oxychloride)

2

4. Derivatives of phosphoric acid (STPP and calcium phosphates)

NOTICE OF ERROR

The following should be substituted for the last two paragraphs on page 3.

It was concluded in the guideline document that for all products under consideration, it was possible to achieve zero water discharge on the basis of best practicable control technology currently available. These two products — phosphorus oxichloride and pentoxide — however, are required to achieve zero water discharge by 1983. For the purpose of analysis, these two products were analyzed for the impact of zero discharge, realizing that the actual cost for 1977 will be lower.

The costs to achieve zero discharge, as presented in the effluent guideline development document, are summarized in Table 1.

III. COSTS

Manufacturing costs were estimated for each of the products under consideration, based on available information on investment and operating costs for plants producing each of the products. Representative plant sizes were selected on the basis of typical plants currently operating, but it was also realized that substantial variation in costs do exist, depending not only on plant size and age, but also on other factors, such as whether or not the production units are included in large multiproduct complexes, or operated independently.

The costs of water pollution control were taken, at the request of EPA, from an effluent guideline development document prepared for that agency. It was not within the scope of this impact analysis study to confirm or modify the water pollution control costs presented in the effluent guidelines development document.

It was concluded in the guideline document that for all products under consideration, it was possible to achieve zero water discharge on the basis of best practicable control technology currently available. Therefore, pollution control costs used in this impact analysis were based on this single level of technology.

The costs to achieve zero discharge, as presented in the effluent guideline development document, are summarized in Table 1.

TABLE 1

COST OF ACHIEVING ZERO DISCHARGE

| Product | Cost (\$/ton) |
|-----------------------------------|------------------|
| Phosphorus | \$4.60 |
| Phosphoric Acid (75%) | 0.65 |
| Phosphorus Pentoxide | 1.40 |
| Phosphorus Pentasulfide | 1.70 |
| Phosphorus Trichloride | 1.40 |
| Phosphorus Oxychloride | 1.25 |
| STPP | 0 |
| Dicalcium phosphate (animal feed) | 1.40 |
| Dicalcium phosphate (food grade) | 1.50 |

^{1.} Cost Information for the Waterborne Wastes in the Non-Fertilizer Phosphorus Chemicals Industry, Supplement A, prepared by General Technologies Corporation.

IV. IMPACT ANALYSIS METHODOLOGY

In assessing the economic impact of the zero discharge costs, as presented in the effluent guideline development document, we took into consideration the fact that some of the products were raw materials for the manufacture of other products covered in this report. Therefore, we included not only the zero discharge costs associated directly with the production of each chemical, but also those arising from zero discharge costs for those raw materials used to make derivative products, where they were included in the list of chemicals covered in this report.

For example, food-grade calcium phosphate is produced from phosphoric acid, in turn manufactured from elemental phosphorus. Thus, we considered the total cost increases arising from the cost of achieving zero discharge in the production of calcium phosphate, in the production of phosphoric acid, and in the production of phosphorus, in analyzing the economic impact of zero discharge on calcium phosphate.

The total costs of achieving zero discharge for each of the products, based on the costs presented in the effluent guideline development document, are summarized in Table 2. Also included in this table is a calculation showing the relation of zero-discharge costs, to current sales prices, for each of the chemicals.

PRICE INCREASES RELATED TO GTC PROPOSED COSTS
OF ACHIEVING ZERO DISCHARGE

| Product | Pollution Control Cost | Raw Material ² Cost Increase | Total Cost Increase | Current ¹ Price | Percentage Increase |
|--------------------|---------------------------|-----------------------------------------|------------------------|-------------------------------|------------------------|
| | (\$/ton) | (\$/ton) | (\$/ton) | (\$/ton) | |
| Phosphorus | 4.60 | | 4.60 | 380 | 1.2 |
| Furnace Acid | 0.65 | 1.10 | 1.75 | 168 | 1.0 |
| Phos. Pentoxide | 1.40 | 1.09 | 2.49 | 400 | 0.6 |
| Phos. Trichloride | 1.40 | 1.09 | 2.49 | 220 | 1.1 |
| Phos. Oxychloride | 1.25 | 1.83 | 3.08 | 245 | 1.2 |
| Phos. Pentasulfide | 1.70 | 1.32 | 3.02 | 267 | 1.1 |
| STPP | / | 1.90 | 1.90 | 162 | 1.2 |
| Feed-grade Dical | 1.40 | | 1.40 | 87 | 1.6 |
| Food-grade Dical | 1.50 | 1.35 | 2.85 | 257 | 1.1 |

1. Prices based on Chemical Marketing Reporter, 7/23/73.

2. Based on following usages:

0.24 tons phos/ton acid

1.09 tons acid/ton STPP

0.24 tons phos/ton pentoxide

0.77 tons acid/ton food-grade dical

0.24 tons phos/ton trichloride

0.29 tons phos/ton pentasulfide

0.19 tons pentoxide + 0.55 tons trichloride/ton oxychloride

V. ECONOMIC IMPACT ANALYSIS

Based on the fact that the costs of achieving zero discharge, as presented in the effluent guideline document, are relatively insignificant in relation to selling price — in no case more than 1.6% of selling price — we conclude that cost increase of this magnitude would have no measurable impact on the production of any of the products covered in this report.

However, one product — STPP — faces the prospect of a substantial decline in market volume, as the use of this product in detergent formulations appears likely to continue to decline. Therefore it is likely that some reduction in productive capacity will take place, primarily due to reduction in demand, that may result in some plant closings. Decisions regarding such plant closings may be influenced by investments that are necessary to achieve zero discharge.

While the effluent guideline development document indicates no net increase in operating cost for achieving zero discharge in the production of STPP, it does assume that some new investment may be necessary, which would be offset over a period of time by recovery of a salable product. Faced with declining markets, certain STPP producers may be reluctant to make this mandatory investment, and this may influence decisions regarding plant shutdowns.

Apart from this factor, the costs presented in the effluent guideline development document would not appear to have any significant economic impact on any of the products covered. Cost increases of this magnitude will either be absorbed, or, more likely, passed on to consumers through price increases. The products covered in this report have rather specific use requirements based on their chemical properties, and are not easily susceptible to replacement or substitution by other products.

If actual costs to achieve zero discharge are significantly higher than indicated in the effluent guideline development document, as a number of producers believe to be the case, significant economic impacts may be felt. However, based on zero-discharge costs used for this report, we do not expect them to cause directly any plant closings, to lead to unemployment in any of the segments examined, or to have any significant impact on communities where production facilities are located.

SECTION II, DESCRIPTION OF INDUSTRIAL PHOSPHATE INDUSTRY

I. OVERALL INDUSTRY

That sector of the phosphate industry which is covered by this study generally consists of phosphorus and its principal nonfertilizer derivatives. Specifically, the products include the following, grouped into the four segments we have selected:

- 1. Phosphorus (P₄)
- 2. Anhydrous Derivatives of Phosphorus
 - a. Phosphorus Pentoxide (P2O5)
 - b. Phosphorus Trichloride (PCl₃)
 - c. Phosphorus Oxychloride (POCl₃)
 - d. Phosphorus Pentasulfide (P4 S10)
 - e. Ferrophosphorus
- 3. Phosphoric Acid Derived from Phosphorus (Furnace Acid)
- 4. Major Derivatives of Furnace Acid
 - a. Sodium Tripolyphosphate (STPP)
 - Calcium Phosphates (excluding fertilizers, and defluorinated phosphates).

The sector of the chemical industry producing these products has the following significant characteristics:

- For the most part, the derivatives of phosphorus are manufactured by the same companies that produce elemental phosphorus.
- The producers of elemental phosphorus are, with two exceptions, large chemical or petroleum companies for whom phosphorus and derivatives represent only a small percentage of total sales.
- A large proportion of the products in this sector are used internally within the producing company for the production of other products and are not sold on the open market.

This last factor — the largely internal use of many of the products in this sector — makes it difficult to estimate the specific profitability of individual products, even for the companies producing them. They are generally included in a much larger range of products grouped together as a profit center and individual profitabilities are often not calculated for these specific products in this sector.

To give some perspective to the industrial phosphate sector, we have prepared a company – product matrix, in Table 3.

A. SEGMENTATION

Primarily because of similar technology, we have broken down the industry sector which is the subject of this proposal into four segments, by product groupings. They are as follows:

1. Phosphorus

This is produced in an electric furnace operation. Except for size, there is relatively little difference among the several furnaces operating in Florida, in Tennessee, and in the western United States.

2. Anhydrous Phosphorus Derivatives

The technology for producing phosphorus pentoxide, phosphorus trichloride, phosphorus oxychloride, and phosphorus pentasulfide, is generally similar in that all involve reaction with other chemicals under anhydrous conditions. The volumes involved in the production of these products are comparatively small in relation to other chemicals examined.

3. Furnace Phosphoric Acid

This is by far the largest volume use for elemental phosphorus. The production of acid involves an oxidation and absorption step. Plants for producing furnace acid are fairly standard and similar.

4. Derivatives of Furnace Acid

The production of sodium tripolyphosphate, and of the various calcium phosphates, are generally similar and involve the aqueous reaction of phosphoric acid with inorganic chemicals such as soda ash or lime. With the exception of one plant using wet process acid, all STPP is manufactured from furnace acid. Most feed-grade dicalcium phosphate is manufactured from wet process acid, while most technical calcium phosphates and all food grades are produced from furnace acid.

TABLE 3

PRODUCERS OF PHOSPHATE PRODUCTS

| | Phosphorus | Phospherus Pentoxid | Phosphorus Trichloride | Phosphorus Oxychloride | Phosphorus Pentasulfide | Furnace | Sodium Tripolyphosphate | Dicalcium | Dicalcium Calcium |
|-------------------------------------------------------------|-------------|------------------------|---------------------------|---------------------------|----------------------------|---------|----------------------------|-----------|-------------------|
| Holmes Company | 00 | | • | 0 | | 0 | 0 | | |
| Mobil Corporation | | | • | | | • | 0 | | |
| Morrotto Company | | | • | 0 | , | • | . 0 | | 0 |
| Occidental Petroleum Corp. | | • | 0 | • | • | 0 | • | • | |
| Stauffer Chemical | 0 0 | 0 | • | • | 0 | 00 | 0 | | 0 |
| TVA Olin Corporation | • | | | | | | 0 | | |
| Goodpasture, Inc. American Cyanamid Co. | | | | | | • | | 0 | |
| Borden, Inc. | | | | | | | | • | • |
| Eastman Kodak Co. Farmland Industries | | | | | | | | 00 | |
| International Minerals & Chemical Corp. Knox Gelatine, Inc. | nical Corp. | | | | | | | | 00 |
| Richardson-Merrell, Inc. | | | | | | | | | • |

B. RELATIVE IMPORTANCE OF EACH SEGMENT

The following table gives some perspective on the relative production capacity for each of the major segments and products as well as the number of plants in operation.

Product Volume

| Product Segment | Approximate Production, 1971 (000/tons) | Number of Plants |
|-----------------------------|-----------------------------------------|------------------|
| Phosphorus | 545 | 10 |
| Furnace Acid | 954 | 21 |
| Anhydrous Derivative | s 151 | 20 |
| Furnace Acid Derivati | ives | |
| STPP | 1040 | 15 |
| Feed-Grade | | |
| Dicalcium Phospha | te 592 | 8 |
| Technical Calcium | | |
| Phosphates | 50 | 6 |

It should be noted that there is some duplication in the location of plants, in that many of these products are produced in integrated chemical complexes which in many instances produce more than one of the products listed above. Therefore, in terms of plant locations, there are fewer than would be indicated by simply adding the number of plants for the product segments included above.

C. TYPES OF FIRMS

For the most part, the products included in this section of the phosphate industry are produced by divisions of large chemical or oil companies. The principal companies involved in the manufacture of most of these products are characterized in Table 4, in terms of annual sales, total number of plants, indicative estimate of the number of major products produced, and the number of employees. It can be appreciated that the products involved in this sector in the case of all of these companies represent only a small fraction of their total manufacturing operations.

We discuss in the following section individual characteristics of each of the four segments chosen. However, it should be appreciated that there is an unusually close interrelationship between the segments. There may be production facilities for products from two or three of the segments in a single chemical complex.

Furthermore, a very large part of the production of the chemicals included is used by a single producing company for the production of other of the chemicals discussed. Therefore, a major volume of the product is transferred internally within a single company rather than being sold commercially on a company to company basis.

TABLE 4

COMPANY DATA

| | 1972 Sales (\$ million) | No. of Plants | No. of Products | No. of Employees |
|------------|----------------------------|---------------|------------------------------------------------------------------|------------------|
| FMC | 1,497.7 | 85 | 220 major products | 46,000 |
| Mobil | 10,295.1 | 120* | More than 200 major products, plus a full line of petroleum prod | 75,600 ucts |
| Monsanto | 2,225.4 | 85 | 71 major products | 63,000 |
| Occidental | 2,720.8 | 92* | More than 200 major products, plus a full line of petroleum prod | 33,000 ucts. |
| Stauffer | 544.2 | 103 | 62 major products | 10,300 |
| Olin | 1,098.3 | 80 | 300 major products | 29,000 |
| Cyanamid | 1,358.9 | 109 | 120 major products | 41,400 |
| Borden | 2,192.9 | 147 | 200 brands | 48,000 |
| IMC | 491.2 | 71 | 60 principal products | 7,000 |

^{*}Excluding pipeline and drilling facilities.

These two facts make it particularly difficult to determine individual product profitabilities. This is true not only because it is impossible to determine individual companies transfer pricing policies but also because the companies themselves in many instances do not look at the individual products as separate profit centers, and do not attempt to calculate or keep track of the profitability of the individual product or product segment.

Nevertheless, we have presented indicative cost data in the following sections to give an approximate idea of the economics of manufacture and sale of the specific products.

It should be pointed out that we have not discussed ferrophosphorus as an individual product. This is a by-product in the manufacture of elemental phosphorus. According to information from the producers, there are no water pollution problems uniquely associated with ferrophosphorus since no water is involved in its recovery or handling. The general aspects relating to the use and disposal of water in electric furnace operations are discussed under Phosphorus.

D. TYPES OF PLANTS

For the most part, the types of plants operated in each of the four segments discussed in this report are generally similar from company to company with principal variations occurring in size of plant, and age. More specific characteristics of the plants are discussed under the individual segment sections.

The one major exception to the generally uniform nature of plants is the fact that one plant, that operated by Olin Corporation, produces sodium tripolyphosphate from wet process acid rather than from furnace acid. The use of the wet process for producing phosphoric acid in this plant, presents quite a different range of water pollution problems, compared to a plant for producing phosphoric acid from phosphorus.

We have discussed the number of employees involved in each segment section. For this overall sector of the industry, it seems clear that the number of employees in the phosphorus segment is an order of magnitude higher than the employees involved in the production of the other three product segments. Total employment in the phosphorus segment may exceed 3,000 employees, while employment in each of the other segments is estimated to be substantially under 1,000.

E. FINANCIAL CONSIDERATIONS

It is important to note the highly integrated nature of that sector of the industry in which these four product segments are involved. The high degree of interrelationship between the various product segments makes a profitability analysis of any one segment difficult.

Sensitivity to price increases arising from water pollution control costs would have two major aspects. The first would be the differential increases among individual companies. Companies with above average pollution control costs would be put at a competitive disadvantage to those companies with lower costs.

The second aspect to price sensitivity would relate to the vulnerability of the specific products or class of plants to substitutable materials. In almost all cases, there is a very specific requirement for the final derivatives covered in this report, and it is unlikely that there would be direct substitution by alternate products. However, there is the possibility that some of these products could be produced in new plants from wet process acid at prices that would be competitive with furnace acid, particularly if there are substantial cost increases arising from pollution control measures.

There is only one plant in the United States producing industrial phosphates from wet process acid — the plant of Olin at Joliet, Illinois. This plant is about 40 years old and uses a rather conventional series of crystallization and filtration steps to produce products of a desired purity.

An alternative type of process has been under consideration by a number of companies. This involves the purification of wet process acid via the solvent extraction route. There are indications that these processes, which are still under development, may permit the production of the industrial phosphates at costs competitive with productions from furnace acid. Interest in these processes would be greatly stimulated if there were indications that the cost of products produced via the furnace acid route were to increase substantially because of pollution control measures.

However, since these processes are still under development and are of a highly proprietary and confidential nature, it is difficult to get information with any precision on the costs of this alternate route to the derivatives with which we are concerned in this report.

II. PHOSPHORUS

A. SEGMENT DESCRIPTION

Phosphorus is universally produced in all electric furnace operation, from phosphate rock. Phosphate rock, sometimes processed into nodules, is blended with coke and occasionally with silica. This mixture is then added to the electric furnace. Electric power is introduced through vertical electrodes and serves to provide the heat necessary for the reaction to take place. The coke reduces the phosphate content of the phosphate rock to elemental phosphorus which passes from the furnace as a gas along with carbon monoxide. Phosphorus is condensed by cooling, is filtered, and stored. Because it oxidizes on contact with the air, phosphorus is generally stored and transported under a water blanket.

A small amount of iron is contained in the phosphate rock, and combines with phosphorus to form ferrophosphorus. This sinks to the bottom of the furnace crucible and is tapped periodically as a molten material. It solidifies, is cleaned, graded, and stored for future shipment.

A slag forms in the process, consisting of the non-phosphatic components of the phosphate rock, and silica. This is also tapped as a liquid, cooled and broken up by water cooling, and used as a construction aggregate material.

Phosphorus is used entirely for the production of various phosphate chemicals, most of which are included in the other segments of this report.

Phosphorus is a solid at normal temperatures but is readily liquefied by heating to approximately 45° centigrade.

Phosphorus furnaces in the United States are generally of quite similar design although they range in size from smaller units with a capacity of approximately 10,000 tons of phosphorus per year, to the larger furnaces producing as much as 45,000 tons per year. In many instances several phosphorus furnaces are grouped together in a production complex although single furnace installations are in operation.

B. PLANTS AND COMPANIES

There are six companies producing phosphorus in the United States. In addition, the Tennessee Valley Authority (TVA) an agency of the U.S. Government is also a major producer.

Table 5 lists those companies producing phosphorus, together with the number of furnaces estimated in operation together with their capacity.

TABLE 5
PHOSPHORUS PRODUCERS

| Company | Location - | Number Operating Furnaces | Operating Furnace Capacity, Tons P ₄ |
|-------------------|-------------------------|------------------------------|----------------------------------------------------|
| Holmes Company | Pierce, Florida | 2 | 20.000 |
| FMC Corporation | Pocatello, Idaho | 4 | 145,000 |
| Mobil Chemical | Nichols, Florida | 1 | 5,000 |
| Monsanto Company | Soda Springs, Idaho | 3 | 110,000 |
| | Columbia, Tennessee | 6 | 135,000 |
| Hooker Chemical | Columbia, Tennessee | 3 | 60,000 |
| Stauffer Chemical | Silver Bow, Montana | 2 | 42,000 |
| | Tarpon Springs, Florida | 1 | 23,000 |
| | Mt. Pleasant, Tennessee | 3 | 45,000 |
| TVA | Muscle Shoals, Alabama | 3 | 40,000 |
| | | | 658,000 |

It can be seen that phosphorus production is concentrated in three general areas, associated with the nearby availability of phosphate rock. These are in Florida, in Tennessee, and in the Idaho-Montana area.

Because phosphorus plants are generally located because of raw material considerations rather than market locations, and because phosphorus is the most economic form in which to transport phosphate values, production of the derivatives of phosphate is generally undertaken at locations other than where the electric furances are located. The exceptions to this are Stauffer Chemical Company at Silver Bow, Montana, Occidental at Columbia, Tennessee, and the TVA at Muscle Shoals, Alabama. At these locations, phosphoric acid is also produced.

However, as shown in the company-product matrix in the previous section, five of the six companies producing phosphorus also produce at other locations phosphoric acid, sodium tripolyphosphate, and certain of the anhydrous phosphorus derivatives. The Holmes Company, which acquired their phosphorus furnace from Continental Oil, is the only company which produces only phosphorus and no derivatives.

It is important to note that because of this configuration of the industry, most elemental phosphorus is shipped substantial distances after manufacture to locations where it is processed into derivatives. As mentioned, it must be shipped under a blanket of water. The volume of water which is used to blanket the phosphorus both in transportation and handling becomes contaminated with phosphorus, and is therefore one aspect of water pollution concern which must be kept in mind.

In the manufacture of phosphorus, there appear to be two general water pollution problems. The first involves so called "phossy" water – water containing suspended phosphorus. Several water streams in the plant that pick up phosphorus are combined and generally treated by means of settling ponds.

A more serious problem in the production of phosphorus relates to the water treatment effluent both from the burden preparation facilities and also from water scrubbing of the effluent gases. Fluorides are a particular problem. The incoming phosphate ore contains about 3% fluoride. Approximately 20% of this is volatilized both in the burden preparation and in the furnace itself, and ends up in the waste treatment water. The remaining 80% of the fluorine is contained in the by-product slag. It is believed that there are some plants which have a total recycle for the scrubber water whereas others may go only part way and may be in fact discharging some fluorine.

It is difficult to generalize on the types of firms or plants that would be particularly affected by water pollution control measures. With the exception of the Holmes Company in Florida, phosphorus is manufactured as a minor portion of much larger enterprises and thus corporate characteristics would have little relevance to water pollution control impact.

As to the location of the phosphorus furnaces — generally concentrated in Florida, Tennessee, and the Idaho-Montana regions — it is also difficult to identify one area or another that would expect a moderately different impact from water pollution control measures. It is true that phosphate rock mined in Tennessee is generally beneficiated by washing, and effluent wash water has been identified as a major pollutant. However, these mining operations are generally quite separate from production of phosphorus, and do not lie within the scope of this segment.

The labor force in a phosphorus furnace operation is relatively high per unit of product, compared with other operations in the chemical industry. It appears that the labor force at a typical multifurnace phosphate operation will range from 250 to 600. Preliminary estimates would indicate that at the 10 locations where phosphorus is produced, involving some 26 furnaces, somewhere in the neighborhood of 3,000 men might be employed directly associated with the production of phosphorus, but not including mining operations. This would appear to be the largest labor force by far of the four segments included in this study.

C. FINANCIAL PROFILE

Since phosphorus is produced at locations where, with one exception, no other products are manufactured, the complications of attempting to allocate costs to calculate profits in a large multiproduct complex are not a factor in examining the financial profile for phosphorus. However, a very large proportion

of phosphorus produced is consumed at other locations by the same company. Therefore, the profitability of phosphorus production in these instances should probably be judged by examining the transfer price, which generally is not available for individual companies. The proportion being sold on the open market is sufficiently small that it does not represent a meaningful indication of the average income being received by the phosphorus producing unit. However, lacking other data, this is probably the best available measure of income for a phosphorus production unit.

As a preliminary indication of the financial profile for the production of phosphorus we present in Table 6, an estimate of the cost of manufacturing phosphorus in Tennessee including depreciation, and typical input costs.

There is a fairly wide range in cost of the major variable costs for phosphorus production particularly regarding electric power. These range from 2.3 mills per kwh for power from the Bonneville Power Administration in Montana to an estimated 7.26 mills for power supplied by the Tampa Electric Company to some of the operations in Florida. This difference of 4.93 mills per kwh is equivalent to about \$59.00/ton of phosphorus.

The cost of phosphate rock is another cost which varies substantially between one operation and another. This cost is much more difficult to ascertain because for the most part phosphate rock is mined by the phosphorus producer and transferred at an unknown price to the phosphorus furnace operation.

There is less variation in the cost of coke, but this again will lead to some variation in the cost of production. Producers in the Tennessee and Florida area are believed to be paying around \$23.00 to \$26.00 per ton of coke delivered. Producers in Idaho and Montana are paying an estimated \$35.00 per ton, currently.

The price of phosphorus is obviously the most important single item affecting profitability. Factors affecting price will be discussed in more detail in the following section. However, the fact that over 90% of phosphorus produced is transferred within the producing company to other chemical manufacturing facilities, makes it extremely difficult to ascertain what in effect was the net income for the individual plants.

The Department of Commerce, in its statistics on inorganic chemical production, permits calculation of an average annual f.o.b. price for phosphorus. This is probably the best indication of price, but still leaves the possibility open that the transfer prices established by the companies on the one hand might be somewhat arbitrary and artificial in nature.

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TABLE 6

ESTIMATED COST OF ELEMENTAL PHOSPHORUS MANUFACTURE

Basis: Three (3) electric furnaces rated at 35,000 KW each,

producing a total of 72,700 tons of P4 per year

Location: Tennessee

Capital Investment: \$45 million

Manufacturing Cost

| Cost Item | Units | Units/Ton P4 | Cost/Unit | Cost(\$)/Ton P4 |
|----------------------------------------------------------|-------|--------------|-----------|-----------------|
| Raw Materials: | | | | |
| Tennessee matrix (26% P ₂ O ₅) | tons | 10.0 | 5.20 | 52.00 |
| Silica | tons | 0.45 | 1.98 | 0.89 |
| Coke | tons | 1.42 | 25.00 | 35.50 |
| Electrodes | lbs | .42 | 0.32 | 13.44 |
| Utilities: | | | | |
| Electricity | kwh | 12,500 | 0.0068 | 85.43 |
| Water | Mgal | 20 | 0.05 | 1.00 |
| Fuel | MSCF | 12 | 0.23 | 2.76 |

| | Cost(\$)/Year | Cost(\$)/Ton P ₄ |
|----------------------------------------|---------------|-----------------------------|
| Salaries, Wages, and Overhead | 3,500,000 | 48.14 |
| Operating Supplies | 400,000 | 5.50 |
| Maintenance | 4,000,000 | 55.02 |
| Taxes and Insurance (2% of investment) | 900,000 | 12.38 |
| Depreciation (6.67% per year) | 3,001,500 | 41.29 |
| Total | | 353.35 |
| By-products credits | | -19.00 |
| Net manufacturing cost | | 334.35 |

Using the cost figure indicated above, plus an arbitrary charge for GS&A of \$35.00/ton the profitability can be estimated for various phosphorus prices. This is presented in Table 7. This shows that with an average cost of \$370 per ton of phosphorus as a manufacturing cost, including GS&A, the profitability after taxes ranges from \$5 with a \$380/ton phosphorus price, f.o.b. plant, to \$25/ton at a \$420/ton selling price. Using an estimated fixed investment of \$620/ton, the after-tax return, as a percentage of fixed assets, ranges from 0.8% at \$380 phosphorus, to 4.0% at \$420 phosphorus.

This table is useful only to indicate the sensitivity of profitability to price of phosphorus. Our estimates of the cost of manufacture have been for one specific hypothetical furnace operation in Tennessee, and wide variations between plants can be expected on the basis of increases in power costs, coke costs, phosphate rock costs, operating rate, etc. This table is not in any sense to be taken as a representative estimate of the profitability of the phosphorus industry.

As an indication of the wide swings which prices have taken in recent years, we present in Table 8 the average value of phosphorus shipment as reported by the U.S. Department of Commerce in their publication, "Current Industrial Reports – Inorganic Chemicals," series M28 A-14.

More recent trade information indicates that phosphorus prices have risen sharply recently. Current commercial sales are reportedly being made at a level of 21¢ per pound, equivalent to \$420.00/ton.

As can be seen from the figures in Table 6, raw material and utility cost present about 57% of the total direct manufacturing costs for phosphorus. This means that the portion of total costs which would be affected by added water pollution costs would be less than 50% of the total. Thus, the leverage on total manufacturing costs of added investment and operating costs necessary for water pollution control would be less than in processes where the raw materials were not such a major factor in manufacturing costs.

The salvage value of a phosphorus installation is likely to be negative — that is, the cost of dismantling and disposing of the facilities would probably be greater than any credits for equipment re-use or resale.

D. PRICES AND MARKETS

It is important in examining the pricing situation regarding phosphorus to appreciate the largely captive nature of phosphorus movements. Over 90% of the phosphorus produced by the six companies, and the TVA, is used within the producing organization (although generally at other locations) for the production of phosphoric acid and phosphorus derivatives.

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TABLE 7

SENSITIVITY OF PHOSPHORUS PROFITABILITY (dollars per ton)

| Price of Phosphorus/Ton | | \$380 | \$400 | \$420 |
|------------------------------------------------|-------------------|-------|-------|-------|
| Cost of Manufacture | | | | |
| Direct Cost GS&A | \$335.00 35.00 | | | |
| | | 370 | 370 | 370 |
| Profit Before Taxes | | 10 | 30 | 50 |
| Profit After Tax | | 5 | 15 | 25 |
| After Tax Return (% on assets) ¹ | | 8.0 | 2.4 | 4.0 |

^{1.} Basis: \$620/annual ton

TABLE 8

RECENT PHOSPHORUS PRICES (\$/ton f.o.b. plant)

| | All Shipments ¹ | Commercial Shipments |
|------|----------------------------|----------------------|
| 1968 | \$336 | \$300 |
| 1969 | 356 | 329 |
| 1970 | 358 | 287 |
| 1971 | 381 | 356 |

^{1.} Both intracompany and intercompany.

Source: U.S. Department of Commerce "Current Industrial Reports – Inorganic Chemicals," Series M28A-14.

^{2.} Intercompany only.

The Department of Commerce in its Bulletin M28-14, reports monthly and annual movements of phosphorus both in total, and for commercial sales alone. These have been presented earlier in Table 8. Along with tonnages, total values are indicated. This is generally considered a good measure of the actual prices at which phosphorus does move.

In Table 8, we have listed the average value per ton of phosphorus for the period from 1968 to 1971 for both total shipments and for commercial sales. It is interesting to note that the value of commercial sales has been consistently below the value of total shipments. Since 90% of the total is represented by intracompany shipments, the value for total movements is very close to that of intra-company movements.

Because they represent only a small portion — less than 10% — of total phosphorus production — commercial sales can expect to show fairly wide fluctuation in prices since this small sector of the total production would be expected to reflect any overall supply/demand imbalance that might develop. In other words in periods of over-capacity, prices on the open market would be expected to drop substantially and in periods of shortages to rise significantly.

The prices for intra-company shipments as in most internal transfer situations, is arbitrary to a degree. Often such transfer prices particularly between separate divisions of a company, are set by policy at the prevailing price in the open market. However, this does not appear to be the case in phosphorus since intra-company shipments have consistently been substantially higher than open market prices.

Because of the somewhat arbitrary nature of intra-plant transfer values, it will be difficult to assess the effect of water pollution control costs on this particular price. Increases in costs will undoubtedly be reflected in increased prices of the ultimate derivatives, although not necessarily properly reflected in the reported transfer prices, as in the Department of Commerce Series M28 A-14.

There is no alternative to phosphorus in the production of its derivatives. Therefore, there is no sensitivity to price in the direct demand for phosphorus itself. There may however, be some sensitivity to price in the demand for some if its derivatives, and this will be reflected ultimately in the demand for phosphorus.

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III. FURNACE PHOSPHORIC ACID

A. SEGMENT DESCRIPTION

Phosphoric acid can be produced by two quite different processes. The first — the "wet process" route — involves the treatment of phosphate rock with sulfuric acid and the subsequent filtration of solid gypsum, to produce a relatively crude phosphoric acid. The second route, which produces a purer acid, involves burning elemental phosphorus to form phosphorus pentoxide, and then absorbing this in water to form phosphoric acid.

With minor exceptions, wet process acid is generally used for the production of various liquid and solid fertilizer materials while phosphoric acid produced from phosphorus or "furnace acid" is predominantly used for the production of various industrial phosphate products. Nevertheless, there is one plant in the United States producing industrial phosphates from wet process acid, and some small use of furnace acid in liquid mixed fertilizers.

Almost all of the furnace acid produced in the United States is manufactured by the producers of phosphorus. All producers except the Holmes Company also produce furnace acid and other derivatives.

Furnace acid is used primarily for the production of a wide variety of phosphate chemicals, principally salts of sodium, potassium, and calcium. The material produced in largest volume from furnace acid is sodium tripolyphosphate, for the detergent market. Its production and that of other calcium phosphates is covered in the fourth segment of this industry sector.

Only two furnace acid plants are located adjacent to a phosphorus furnace; that of Stauffer in Silver Bow, Montana, and Occidental's plant at Columbia, Tennessee. All other phosphorus production used to make acid is shipped to other locations.

B. PLANTS AND COMPANIES

There are estimated to be 23 furnace acid plants in the United States. Twenty-one of these are operated by basic phosphorus producers. One plant in Texas uses purchased phosphorus. Acid plants are listed in Table 9 with their locations, and total company capacity. Individual plant capacities were not available at the time of writing this draft.

As in the case of phosphorus, it is difficult to identify types of firms or types of plants, involved in the production of furnace acid, that would be impacted to a greater or lesser degree by water pollution control measures. Furnace acid plants

TABLE 9

LOCATION OF FURNACE ACID PLANTS

| Producers | Plant Location | Grouped Company Capacity |
|----------------------------|---------------------------|---------------------------------------|
| | | (tons P ₂ O ₅) |
| FMC Corporation | Carteret, New Jersey | |
| | Lawrence, Kansas | 340,000 |
| | Newark, California | |
| | Green River, Wyoming | |
| Mobil Oil Corporation | Carteret, New Jersey | 115,000 |
| | Fernald, Ohio | |
| Monsanto Company | Augusta, Georgia | |
| | Carondolet, Missouri | 455,000 |
| | Kearny, New Jersey | |
| | Long Beach, California | |
| | Trenton, Michigan | |
| Occidental Petroleum Corp. | Dallas, Texas | |
| | Jeffersonville, Indiana | 85,000 |
| | Columbia, Tennessee | |
| Stauffer Chemical Company | Chicago, Illinois | |
| | Chicago Heights, Illinois | |
| | Morrisville, Pennsylvania | |
| | Nashville, Tennessee | 250,000 |
| | Richmond, California | |
| | Silver Bow, Montana | |
| | South Gate, California | |
| TVA | Muscle Shoals, Alabama | 75,000 |
| Goodpasture, Inc. | Brownfield, Texas | 45,000 |
| Total | | 1,365,000 |

are generally located close to concentrated markets and thus tend to be placed in more densely populated areas than phosphorus furnaces for example.

The labor force for an individual furnace acid plant is not large. If operated as an independent unit and not as part of a complex, the labor force for a furnace acid plant might vary from 20 to 40 people depending on size. If included in a complex of several plants, the labor component might be significantly less. Assuming an average of 30 men per plant, with some 20 furnace acid plants in operation, a total industry force in this segment of some 600 could be approximated.

The technology is generally quite similar for all of the furnace acid plants with the major difference lying in the lining of the furnace in which phosphorus is burned to phosphorus pentoxide. In the older plants, these were lined with carbon bricks, which were cooled by dribbling cooling water over them. This led to some pickup of the phosphorus pentoxide in this cooling water resulting in contamination of this water with phosphoric acid.

All of the more recent plants that have been built substituted a stainless steel water cooled jacket for the carbon brick, and cut down to a very high degree on this contamination of the cooling water. In all other aspects we believe that all of the furnace acid plants are generally quite similar.

C. FINANCIAL PROFILE

As pointed out previously, in the entire group of phosphorus based products being examined in this report, there is a great deal of vertical integration with most products being produced by companies that either manufacture the basic raw materials or consume the products themselves in the further manufacture of other derivatives. (Thus, we are faced with the problem of estimating or ascertaining intra-company transfer values rather than examining open market prices.) This is particularly confusing in the case of the products like furnace acid, where both the raw material input — in this case phosphorus — and the final product — furnace acid — are generally transferred on an intra-company basis.

On the other hand, the financial analysis of furnace acid manufacture is greatly simplified by the fact the cost of the basic raw material – phosphorus – the overwhelmingly most important cost component in the overall manufacturing cost of furnace acid, comprises approximately 94% of the final cost. Thus, any increases in process costs that might arise because of water pollution control measures, even if relatively substantial, would have only a minor effect on the overall cost of manufacturing furnace acid.

We show in Table 10 the representative breakdown of the cost of making furnace acid. We have used the current list price for open market purchases of phosphorus of \$380.00 per ton although we believe that current spot sales are actually being made substantially above this.

Prices for furnace acid currently are well below this calculated cost of manufacture and have been for recent years. This suggests that phosphorus is being transferred into the furnace acid plants at substantially below the list price, although the Department of Commerce figures for intra-company do seem to indicate the transfer at essentially list. This would indicate that the furnace acid plants are operating at or below the manufacturing cost on this transfer basis.

D. PRICING

As in the case of phosphorus, only a small percentage of furnace acid produced is sold on the open market to other companies. Almost all is used internally by the producer for the manufacture of other derivatives. Furthermore, only about 25% of production is shipped from the point of production to another plant. It is only this portion that is reported by the Department of Commerce in a way in which its value f.o.b. plant can be calculated. However, we have extracted these figures for the years of 1968 to 1971, summarized below:

Furnace Acid Values (\$/ton P₂ O₅, f.o.b. plant)

| 1968 142.00 1969 165.00 1970 156.00 1971 168.00 | | Value per Ton P ₂ O ₂ |
|-----------------------------------------------------------------------------------|------|---------------------------------------------|
| 1970 156.00 | 1968 | 142.00 |
| 100.00 | 1969 | 165.00 |
| 1971 168.00 | 1970 | 156.00 |
| [18] [18] [18] [18] [18] [18] [18] [18] | 1971 | 168.00 |

It is interesting to note that all of these prices are substantially below the direct manufacturing cost of furnace acid, calculated from a typical recent transfer value of phosphorus of \$380.00. This underlines again, the somewhat arbitrary and unreliable nature of the reported intracompany transfer figures as a reflection of true price and realistic profitability.

For two reasons, it is unlikely that the effects of water pollution control costs will be major or significant in terms of furnace phosphoric acid. In the first place, over 90% of the cost of furnace acid, as mentioned above, consists of the cost of phosphorus and the effect of major changes of water pollution control costs associated directly with the manufacture of acid would not be particularly significant. Furthermore, since most of furnace phosphoric acid involves

TABLE 10

ESTIMATED COST OF MANUFACTURING PHOSPHORIC ACID FROM ELEMENTAL PHOSPHORUS

Basis: 54% P2 O5 Phosphoric Paid equivalent to

45,000 tons/year of P2Os

Plant located in Midwestern U.S.A.

Phosphorus cost (f.o.b. furnace plant) at
\$380.00 per ton P₄; freight, \$5.00 per ton P₄

Capital Investment: \$1 million (includes storage for 3,000 tons P2O5;

no P4 storage)

Manufacturing Cost

| Cost Item | Units | Units/Ton P ₂ O ₅ | Cost/Unit | Cost(\$)/Ton P ₂ O ₅ |
|----------------------------|---------------------|-----------------------------------------|-----------|--------------------------------------------|
| Raw Materials and Freight: | | | | , |
| Phosphorus | Tons P ₄ | 0.44 | 380.00 | 167.20 |
| Freight | Tons P ₄ | 0.44 | 5.00 | 2.20 |
| Utilities | | | | |
| Electricity | Kwh | 60 | 0.0068 | 0.41 |
| Water | Mgal | 23 | 0.05 | 1.15 |

| | Cost(\$)/Year | Cost(\$)/Ton P ₂ O ₅ |
|----------------------------------------|---------------|--------------------------------------------|
| Salaries, Wages, and Overhead | 180,000 | 4.00 |
| Operating Supplies | 5,000 | 0.10 |
| Maintenance (4% of investment) | 40,000 | 0.89 |
| Taxes and Insurance (2% of investment) | 20,000 | 0.45 |
| Depreciation (6.67% per year) | 67,000 | 1.48 |
| | | 177.88 |

intra-company transfers of both raw material and finished product, its pricing is somewhat academic.

As in the case of phosphorus with only a small portion of total production moving in open market sales, it is likely that there would be relatively wide fluctuation in the price of this small open market segment reflecting changing supply/demand conditions. As has happened in the past, when there have been substantial surpluses of furnace phosphoric acid, these have moved at relatively low prices primarily into the liquid fertilizer market, to maintain capacity operation at phosphorus furnaces, where costs are quite sensitive to the operating rate. In the same vein, during periods of short supply, quantities available on the open market would be limited and would undoubtedly rise sharply in price. Thus, price fluctuations in open market phosphoric acid are much more likely to depend on the factors related to the supply/demand situation, than on water pollution control costs associated with the acid manufacture.

IV. DERIVATIVES OF ELEMENTAL PHOSPHORUS

A. SEGMENT DESCRIPTION

Four of the products comprising this segment are produced from elemental phosphorus (POCl₃, P₂S₅, P₂O₅, and PCl₃). The fifth, ferrophosphorus, is a by-product of the phosphorus furnace. In fact, ferrophosphorus is not impacted by water pollution abatement considerations and may be appropriately excluded from this segment. The first four derivatives, however, do merit common consideration as a segment because all four are produced under anhydrous conditions and are similarly impacted to the extent that any water pollution aspect exists. Further community of consideration is warranted because several of the four elemental phosphorus derivatives are frequently produced at a common site for both merchant sale or further processing as chemical intermediates.

B. COMPANIES AND PLANTS

The primary producers of the elemental phosphorus derivatives are major components of the U.S. chemical industry, namely FMC Corporation, Hooker Chemical Corporation (subsidiary of Occidental Petroleum Corporation), Mobil Chemical Company (subsidiary of Mobil Oil Company), Monsanto Company, and Stauffer Chemical Company. All of these are integrated back to production of elemental phosphorus. In general these producers are also integrated forward, with the derivatives as intermediates, for synthesis of such end products as pesticides, plasticizers, lube oil additives, flotation agents, and surfactants.

There are also several small specialty chemical producers of the products, primarily for electronic markets, but these represent such a minor part of the segment that their separate consideration is unwarranted.

Two of the five integrated producers of elemental phosphorus derivatives have a single producing location. The others have multiplant locations for the derivatives but may produce only one of the derivatives at a given location. Of the four derivatives considered (POCl₃, P₂S₅, P₂O₅, and PCl₃), both Hooker Chemical Company and Stauffer Chemical produce all four. The other major producers manufacture one to three of them.

The primary plant sites are Nitro, West Virginia; Niagara Falls, New York; Sauget, Illinois; Anniston, Alabama; Charleston, South Carolina; Morrisville, Pennsylvania; Mt. Pleasant, Tennessee; Nashville, Tennessee; and Cold Creek, Alabama.

Ferrophosphorus is drawn off before the slag and it is important that it not come into contact with water with which it may react explosively at this point in the furnace production cycle.

| | Derivatives Manufactured | | | | |
|--------------------------|---------------------------------|----------|-------------------------------|------------------|--|
| Producing Company | POCI ₃ | P_2S_5 | P ₂ O ₅ | PCl ₃ | |
| FMC | × | | | x | |
| Hooker | X | X | X | X | |
| Mobil | | | | X | |
| Monsanto | X | X | | X | |
| Stauffer | X | X | X | X | |

Because most of the plant sites are large multiproduct, integrated operations producing fifty or a hundred individual chemical products, the derivatives of elemental phosphorus within the sector constitute only a small fraction of the plant site output, plant site employment, or plant site water pollution impact. Furthermore, this segment represents only about 5% of the total tonnage of the nonfertilizer phosphate industry which is analyzed in this report.

C. FINANCIAL PROFILE

Because industry manufacturing costs were not made available to us on the derivatives of elemental phosphorus, these were calculated based primarily on our internal engineering estimates. As such, they are presented in the following Tables 11 through 14 for $POCl_3$, P_2S_5 , P_2O_5 , and PCl_3 . It is important to note that for production of P_2S_5 , P_2O_5 , and PCl_3 , the phosphorus is introduced into the reaction at a market price of \$380 per ton delivered. In the case of $POCl_3$, the two phosphorus derived raw materials are also introduced at the published market prices, i.e., \$400 per ton P_2O_5 and \$220 per ton for PCl_3 . It is assumed that both these raw materials for $POCl_3$ are produced at the same plant as the $POCl_3$ and no freight costs are involved.

Using current published selling prices for the four derivatives of elemental phosphorus considered herein, the following estimated plant cash flows may be developed in cents per pound at the plant site.

| | POCI ₃ | P ₂ S ₅ | P_2O_5 | PCl ₃ |
|-----------------|-------------------|-------------------------------|----------|------------------|
| Selling Price | 12.25* | 14.20** | 20.00** | 11.00* |
| Plant Cost | 12.70 | 10.30 | 9.90 | 9.20 |
| Plant Margin | (0.45) | 3.90 | 10.10 | 1.80 |
| Depreciation | 4.10 | 3.41 | 4.55 | 2.53 |
| Plant Cash Flow | 3.65 | 7.31 | 14.65 | 4.33 |

^{*}in bulk

^{**}in carloads of drums.

TABLE 11

ESTIMATED COST OF MANUFACTURING PHOSPHORUS OXYCHLORIDE

| Plant Location | Eastern Onited States |
|-------------------|-----------------------|
| Annual Production | |
| Fixed Investment | \$900,0001 |
| | |

| Variable Costs | Quantity | \$/Unit | \$/Ton |
|----------------------------|----------------------------------|-----------|--------|
| Phosphorus Pentoxide | 0.189 T | 400 | 75.60 |
| Phosphorus Trichloride | 0.548 T | 220 | 120.56 |
| Chlorine | 0.283 T | 70 | 19.81 |
| Power | 25 kwh | 0.01 | 0.25 |
| Cooling Water | 11.1 M gal | 0.03 | 0.33 |
| Steam | 0.73 M lbs | 1.40 | 1.02 |
| Operating Supplies | | | 0.50 |
| | | | 218.07 |
| Semi-Variable Costs | | | |
| Operating Labor | 2 men/shift | 4.50/hr | 7.88 |
| Supervision | 1/2 of 4 foremen | 13,000/yr | 2.60 |
| | 1/2 of 1 super. | 17,000/yr | 0.88 |
| Maintenance | 7½% of Investment/yr | | 3.75 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 3.41 |
| | | | 18.52 |
| | | | |
| Fixed Costs | | | |
| Plant Overhead | 70% of Op. Labor and Supervision | | 7.95 |
| Depreciation | 9.1% of Investment/yr | | 8.19 |
| Local Taxes and Insurance | 11/2% of Investment/yr | | 1.35 |
| | | | 17.49 |
| Total Cost of Manufacture, | Bulk Liquid | | 254.08 |

^{1.} Assumes part of complex receiving cooling water, steam, services, etc. from central facility.

TABLE 12

ESTIMATED COST OF MANUFACTURING PHOSPHORUS PENTASULFIDE

Plant Location East Coast
Annual Production 10,000 tons
Fixed Investment \$750,000¹

| Variable Costs | Quantity | \$/Unit | \$/Ton |
|----------------------------|----------------------------------|-----------|--------|
| Phosphorus | 0.287 T | 380 | 109.06 |
| Sulfur | 0.736 T | 35 | 25.76 |
| Power | 7.8 kwh | 0.01 | 0.08 |
| Water | 1.95 M gal | 0.03 | 0.06 |
| Steam | 0.08 M lbs | 1.40 | 0.11 |
| Operating Supplies | | | 0.50 |
| Drums, 450 lb ea. | 4.45 | 5.73 | 25.46 |
| | | | 161.03 |
| Semi-Variable Costs | | | |
| Operating Labor | 3 men/shift | 4.50/hr | 11.83 |
| Operating and | 2 men days | 4.50/hr | 1.87 |
| Supervision | 1/2 of 4 foremen | 13,000/yr | 2.60 |
| | 1/2 of 1 super. | 17,500/yr | 0.87 |
| Maintenance | 8% of Investment/yr | | 3.20 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 5.15 |
| | | | 25.52 |
| Fixed Costs | | | |
| Plant Overhead | 70% of Op. Labor and Supervision | | 12.02 |
| Depreciation | 9.1% of Investment/yr | | 6.83 |
| Local Taxes and Insurance | 1.4% of Investment/yr | | 1.13 |
| | | | 19.98 |
| Total Cost of Manufacture, | 450 lb drums | | 206.53 |

^{1.} Assumes plant part of complex with steam, water and other services supplied from central facilities.

TABLE 13

ESTIMATED COST OF MANUFACTURING PHOSPHORUS PENTOXIDE

Annual Production 5,000 tons

Eastern United States

Plant Location

| | Fixed Investment \$500,000 | | |
|----------------------------|----------------------------------|-----------|--------|
| Variable Costs | Quantity | \$/Unit | \$/Ton |
| Phosphorus | 0.237 T | 380 | 90.06 |
| Steel Cans | 6.15 | 5.40 | 33.21 |
| Power | 85 kwh | 0.01 | 0.85 |
| Water | 0.6 M gal | 0.03 | 0.02 |
| Steam | nil | 1.40 | - |
| Operating Supplies | | | 0.50 |
| | | | 124.64 |
| Semi-Variable Costs | | | |
| Operating Labor | 2 men/shift | 4.50/hr | 15.77 |
| | 5 men, 200 days | 3.00/hr | 4.80 |
| Supervision | 1/2 of 4 foremen | 13,000/yr | 5.20 |
| | 1/2 of 1 super. | 17,500/yr | 1.75 |
| Maintenance | 7% of Investment/yr | | 7.00 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 8.26 |
| | | | 42.78 |
| Fixed Costs | | | |
| Plant Overhead | 70% of Op. Labor and Supervision | | 19.26 |
| Depreciation | 9.1% of Investment/yr | | 9.10 |
| Local Taxes and Insurance | 1.5% of Investment/yr | | 1.50 |
| | | | 29.86 |
| Total Cost of Manufacture, | Drums | | 197.28 |

TABLE 14

ESTIMATED COST OF MANUFACTURING PHOSPHORUS TRICHLORIDE

Annual Production 9,000 cons

Eastern United States

1.40

1.06

0.30 149.40

Plant Location

Fixed Investment \$500,000¹ Variable Costs Quantity \$/Ton \$/Unit **Phosphorus** 0.237 T 380 90.06 Chlorine 0.815 T 70 57.05 Power 24.5 kwh 0.01 0.25 **Cooling Water** 0.03 22.6 M gal 0.68 Steam 0.76 M lbs

Semi-Variable Costs

Operating Supplies

| Operating Labor | 2 men/shift | 4.50/hr | 8.26 |
|-----------------|----------------------------------|-----------|-------|
| Supervision | 1/2 of 4 foremen | 13,000/yr | 2.89 |
| | 1/2 of 1 super. | 17,500/yr | 0.97 |
| Maintenance | 7%% of Investment/yr | | 4.17 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 3.64 |
| | | | 19.93 |

Fixed Costs

| Plant Overhead | 70% of Op. Labor and Supervision | 8.48 | 8.48 |
|----------------------------|----------------------------------|------|--------|
| Depreciation | 9.1% of Investment/yr | | 5.06 |
| Local Taxes and Insurance | 1½% of Investment/yr | | 0.83 |
| | | | 14.37 |
| Total Cost of Manufacture, | Bulk | | 183.70 |

Assumes plant part of complex receiving cooling water, steam, services, etc., from central facility.

Actual salvage values of the assets of these plants were not determined. It may be expected that specific items such as pumps, piping, centrifugal equipment, etc., will have some salvage value. In general, however, we expect that such salvage value will be less than 25% of capital cost, and frequently much less than 25%.

D. PRICE EFFECTS

The published prices of P₂S₅ and PCl₃ have remained stable for the past five years. Those of POCl₃ and P₂O₅ have risen in the past 2-3 years. The published price of POCl₃ increased about 15% in 1972; that of P₂O₅ about 25% over the longer period of 1971-1973.

While LCL transactions tend to be at published prices, it can be expected that larger volumes are sold at negotiated contract prices covering extended periods of time. Because much of the industry has an internal requirement for part of its capacity to produce the elemental phosphorus derivatives, merchant contract sales may be more advantageous to one seller than another at any given time depending upon that seller's internal requirements. So in general the prices of significant volumes are negotiated prices while lesser volumes are published price transactions.

Published price increases are usually initiated by a major producer and either followed or not by the other producers. If price changes are not followed, the initiator rescinds the price. Because the elemental phosphorus derivatives are produced in large integrated chemical plants where the impact of water pollution control is not readily isolated on a product-by-product basis, the cost of pollution control will result in price increases for selected products only where the general competitive situation permits such increases. Over extended periods increased manufacturing costs of any type generally exert an upward pressure on chemical prices, but changes take place only at those points in time when the competitive aspects permit. In the case of the derivatives of elemental phosphorus, specific price increases directly attributable to pollution control are not expected.

V. DERIVATIVES OF PHOSPHORIC ACID

A. SEGMENT DESCRIPTION

The segment is restricted to (1) the largest volume sodium salt of phosphoric acid, sodium tripolyphosphate, and (2) those calcium phosphates used industrially or in the manufacture of animal feeds. The phosphoric acid from which these derivatives are made can be of either furnace or wet process origin.

Sodium tripolyphosphate (STPP) is generally produced from furnace grade phosphoric acid because of the improved color of its salts. However, there is one major producer, Olin Corporation, which uses wet process acid to produce STPP.

For the production of feed-grade dicalcium phosphates, the general practice is to use wet process phosphoric acid and limestone as the primary reactants. Dentifrice and food-grade calcium phosphates generally use furnace acid.

The traditional market for STPP has been as a detergent builder. Historically, the detergent manufacturers have been responsible for 90% of the STPP consumed in the United States, most of it in household laundry formulations. This market is now threatened by various state and local legislative measures designed to restrict the phosphate content of detergent formulations.

In the case of the calcium phosphates considered within the definition of this segment more than 90% of the consumption is for animal feeds. In addition there are specialty grades suitable for use in dentifrices and as leavening agents in baking.

B. PRODUCING COMPANIES AND PLANTS

1. Sodium Tripolyphosphate (STPP)

Table 15 indicates the manufacturers, their plant locations, and estimated plant capacities for STPP production.

With the exception of the Olin plant at Joliet, Illinois, each of these locations is also a location for furnace acid production. Thus the plants may be considered as integrated operations. The plant locations are determined to a major degree by the amount of freight equalization required to be paid on shipments to major detergent producing plants. Thus the freight on STPP tends to associate

Specifically excluded are fertilizer grades of calcium phosphate and defluorinated phosphate rock.

specific STPP producing locations with specific detergent plants. In fact proximity to the market is the most important factor in determining the location for a furnace acid and STPP complex.

TABLE 15
U.S. PRODUCERS OF STPP

| Company | Plant Location | Capacity 1 |
|------------|---------------------------|-------------------|
| | | (thousands ST/yr) |
| FMC | Carteret, New Jersey | 100 |
| FMC | Green River, Wyoming | -75 |
| FMC | Newark, California | 50 |
| FMC | Lawrence, Kansas | 75 |
| Mobil | Fernald, Ohio | 50 |
| Monsanto | Augusta, Georgia | 50 |
| Monsanto | Kearny, New Jersey | 125 |
| Monsanto | Long Beach, California | 75 |
| Monsanto | Trenton, Michigan | 75 |
| Monsanto | Carondelet, Missouri | 100 |
| Occidental | Dallas, Texas | 35 |
| Occidental | Jeffersonville, Indiana | 100 |
| Olin | Joliet, Illinois | 150 |
| Stauffer | Chicago, Illinois | 40 |
| Stauffer | Morrisville, Pennsylvania | 75 |
| | | 1175 |

^{1.} Subject to significant variation, depending on grades produced.

There is a significant water pollution aspect to the production of STPP because of the wet scrubbing of the dust at various points in the process. To the extent that such water is returned to the system, water pollution is minimized. To the extent which it is not, lime precipitation and clarifiers are required.

2. Calcium Phosphates

Among the nonfertilizer types, dicalcium phosphate, primarily used for animal feed, predominates. Table 16 identifies major producing locations, most of which are located in proximity to either a wet phosphoric acid producing location or the primary feed markets. Capacities are not readily identified because part of the plant capacity in some cases can be utilized for fertilizer grades of calcium phosphate.

The water pollution aspects of feed grade dicalcium phosphate are similar to those of STPP for which wet scrubbing operations are required. Where wet process acid has not been defluorinated there is the additional problem of fluorsilicate disposal. With purified grades for dentifrice and human consumption, the impact is amplified by larger water requirements for manufacture and in the case of anhydrous product, the dewatering process.

TABLE 16

U.S. PRODUCERS OF CALCIUM PHOSPHATES

| Company | Plant Location |
|-----------------|---------------------------|
| Cyanamid | Weeping Water, Nebraska |
| Cyanamid | Alden, Iowa |
| Cyanamid | Hannibal, Missouri |
| Borden | Plant City, Florida |
| Central States* | Weeping Water, Nebraska |
| Eastman Kodak | Peabody, Massachusetts |
| Farmland | Hannibal, Missouri |
| IMC | Bonnie, Florida |
| Monsanto | Carondelet, Missouri |
| Occidental | Davenport, Iowa |
| Occidental | White Springs, Florida |
| Stauffer | Chicago Heights, Illinois |
| Stauffer | Nashville, Tennessee |

^{*}destroyed by fire but currently being rebuilt.

C. FINANCIAL PROFILE

Because industry manufacturing costs were not made available to us for either STPP or feed grade dicalcium phosphate, these have been calculated on the basis of our internal knowledge of the production costs involved.

1. Sodium Tripolyphosphate (STPP)

Table 17 establishes a manufacturing cost of \$224 per ton for an STPP plant operating at a production rate of 50,000 tons per year utilizing furnace acid produced at the same site. The acid transfer price as indicated is \$149 per ton. On this cost basis and using a published selling price of \$162 per ton and \$3 of freight equalization, the estimated plant cash flow is as follows:

| Selling Price | 159 \$/ton |
|-----------------|-------------|
| Plant Cost | 224 \$/ton |
| Plant Margin | (65) \$/ton |
| Depreciation | 4 \$/ton |
| Plant Cash Flow | (61) \$/ton |

TABLE 17

ESTIMATED COST OF MANUFACTURING SODIUM TRIPOLYPHOSPHATE

Annual Production 50,000 T

Midwest 150 T/SD

Plant Location

Plant Capacity

| | Fixed Investment \$2,440,000 | | |
|----------------------------------|----------------------------------|-------------------------------------------|-----------------|
| Variable Costs | Quantity/Ton | \$/Unit | \$/Ton |
| Phosphoric acid, 75% Soda Ash | 1.087 T 0.735 T | 149.00 ¹ 44.50 ² | 161.96 32.71 |
| Operating Supplies | 20 0 lamb | 0.01 | 0.50 0.39 |
| Power Fuel | 38.9 kwh 13.9 MM Btu | 0.80 | 11.12 |
| | | | 206.68 |
| Semi-Variable Costs | | | |
| Operating Labor | 4 men/shift | 4 50/hr | 3.15 |
| Supervision | 4 foremen | 13,000/yr | 1.04 |
| Supervision | 1 super. | 17,500/yr | 0.35 |
| Maintenance | 5% of Investment/yr | | 2.44 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 1.36 |
| • | | | 8.34 |

| Fixed | Costs |
|-------|-------|
|-------|-------|

| Plant Overhead | 70% of Op. Labor and Supervision | 3.18 4.44 |
|----------------------------------------|---------------------------------------------|--------------|
| Depreciation Local Taxes and Insurance | 9.1% of Investment/yr 1.5% of Investment/yr | 0.73 |
| | | 8.35 |
| Total Cost of Manufacture | | 223.37 |

Total Cost of Manufacture

1. FOB plant value, assumes STPP plant at same site as acid plant.

2. \$35.50 FOB plant plus \$9.00 freight.

However, if the phosphoric acid made in the same plant is transferred at cost, or \$96 per ton, a plant cash flow close to breakeven results.

| Selling Price | 159 \$/ton |
|-----------------|------------|
| Plant Cost | 165 \$/ton |
| Plant Margin | (6) \$/ton |
| Depreciation | 4 \$/ton |
| Plant Cash Flow | (2) \$/ton |

If a reasonable GS&A charge of \$3.50 per ton is applied, there is a net loss before taxes of \$10 per ton. Furthermore, the bulk of the sales to the large household detergent producers are generally made below list. For these a net back after freight equalization of \$153 is more realistic than \$159. Under such conditions the net loss before taxes becomes \$7-8 per ton.

Actual salvage values of the STPP were not determined. In general, however, we expect that such salvage value will be less than 25% of capital cost, and frequently much less than 25%.

2. Calcium Phosphates

Table 18 develops the manufacturing cost of a plant manufacturing 65,000 tons per year of feed grade (18.5% P) dicalcium phosphate. Currently this product is in short supply and from Midwest manufacturing locations is priced at \$87.25 per ton in bulk, freight equalized with competitive locations. In order to calculate a typical plant cash flow and profit before tax we have taken \$4.25 as typical freight equalization with a net back to the plant of \$83 per ton. The plant cash flow then becomes:

| Selling Price | \$83 per ton |
|-----------------|--------------|
| Plant Cost | 70 per ton |
| Plant Margin | 13 per ton |
| Depreciation | 2 per ton |
| Plant Cash Flow | 15 per ton |

If the GS&A allowance is \$3 per ton, the profit before tax is \$10 per ton.

Table 19 similarly develops the manufacturing cost for dicalcium phosphate dihydrate which is one of the refined grades. This and other refined grades serve the dentifrice and human food markets. The plant cash flow for dicalcium phosphate dihydrate is characteristically higher than for feed grade dicalcium phosphate.

TABLE 18

ESTIMATED COST OF MANUFACTURING DICALCIUM PHOSPHATE (Feed Grade 18.5% P)

| Plant Location | Midwest |
|----------------|-----------------|
| Annual Produc | ction 65,000 T |
| Fixed Investm | ent \$1,200,000 |

| Variable Costs | Quantity | \$/Unit | \$/Ton |
|-------------------------------------------|----------------------------------|-------------------|--------|
| Defluorinated Phosphoric | | | |
| Acid, P ₂ O ₅ basis | 0.458 T | 125.001 | 54.59 |
| Ground Limestone | .728 T | 9.00 ² | 6.55 |
| Power | 18.2 kwh | 0.01 | 0.18 |
| Water | 0.06 Mgal | 0.05 | - |
| Fuel | 0.1 MM Btu | 0.80 | 0.08 |
| Operating Supplies | | | 0.10 |
| | | | 61.50 |
| Semi-Variable Costs | | • | |
| Operating Labor | 2 men/shift | 4.50/hr | 1.21 |
| | 2 men days | 4.50/hr | 0.29 |
| Supervision | 4 foremen | 13,000/yr | 0.80 |
| | 1 superintendent | 17,500/yr | 0.26 |
| Maintenance | 5% of Investment/yr | | 0.92 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 0.77 |
| | | | 4.25 |
| Fixed Costs | | | |
| Plant Overhead | 70% of Op. Labor and Supervision | | 1.79 |
| Depreciation | 9.1% of Investment/yr | | 1.68 |
| Local Taxes and Insurance | 1.5% of Investment/yr | | 0.28 |
| | | | 3.75 |
| Total Cost of Manufacture, | Bulk | | 69.50 |

 ^{\$110/}T P₂ O₅ plus \$15 freight
 \$4/ton plus \$5 freight.

0

TABLE 19

Midwest

ESTIMATED COST OF MANUFACTURING DICALCIUM PHOSPHATE DIHYDRATE

Plant Location

| | Annual Production 20,000 tons Fixed Investment \$730,000 | | g |
|----------------------------|----------------------------------------------------------|---------------------|--------|
| Variable Costs | Quantity | \$/Unit | \$/Ton |
| Hydrated Lime | 0.453 T | 28.00¹ | 12.68 |
| Phosphoric Acid 75% | 0.774 T | 159.00 ² | 123.07 |
| Cooling Water | 2.3 Mgal | 0.03 | 0.07 |
| Power | 37 kwh | 0.01 | 0.37 |
| Water, Process | 1.25 Mgal | 0.03 | 0.04 |
| Fuel | 1.1 MM Btu | 0.80 | 0.88 |
| Operating Supplies | | | 0.50 |
| Bags | 20.1 | 0.20 | 4.02 |
| | | | 141.63 |
| Semi-Variable Costs | | | |
| Operating Labor | 3 men/shift | 4.50/hr | 5.91 |
| | 5 men, 250 days | 4.00/hr | 2.00 |
| Supervision | 4 foremen | 13,000/yr | 2.60 |
| | 1 superintendent | 17,500/yr | 0.88 |
| Maintenance | 5% of Investment/yr | | 1.83 |
| Labor Overhead | 30% of Op. Labor and Supervision | | 3.42 |
| | | | 16.64 |
| Fixed Costs | | | |
| Plant Overhead | 70% of Op. Labor and Supervision | | 7.97 |
| Depreciation | 9.1% of Investment/yr | | 3.32 |
| Local Taxes and Insurance | 1.5% of Investment/yr | | 0.55 |
| | | | 11.84 |
| Total Cost of Manufacture, | Bagged | | 170.11 |

^{1. \$22} fob plus \$6.00 freight
2. \$149 fob plus \$10.00 freight

| Selling Price | \$230 per ton |
|-----------------|---------------|
| Plant Cost | 170 per ton |
| Plant Margin | 60 per ton |
| Depreciation | 3 per ton |
| Plant Cash Flow | 63 per ton |

With GS&A costs of \$30 per ton the profit before tax is \$33 per ton.

D. PRICE EFFECTS

The published prices of STPP as sold in bulk and shipped in hopper cars, freight equalized with competitive locations, have increased from \$135 per ton in 1967 to \$152 per ton in 1972 to a current level of \$162. Over this same period the major detergent producers have generally paid \$140-\$155. With freight equalization and a generally low level of profitability, most producing plants rely on one or two major volume detergent plants for a majority of their STPP sales and these one or two plants are those for which freight equalization is minimal.

Prices for STPP have been traditionally established by highly competitive bidding for the large annual requirements of such major detergent plants. This bidding process has resulted in low margins and a reluctance on the part of the producers to expand capacity. Currently STPP is in short supply, but because of price controls cannot rise to levels where return on investment is adequate to stimulate expanded production.

If pollution considerations significantly reduce the use of STPP in detergents, the current tight supply situation would be alleviated, and excess capacity might appear. This would produce a downward pressure on prices.

The pricing of calcium phosphates for feed use is complex with major differentials based on geographic location and freight equalization. Thus for the producing point of Bonnie, Florida, which is distant from the major Midwest markets, the price of feed grade dicalcium phosphate is \$74.00 per ton freight equalized. Similarly, at Weeping Water, Nebraska, for a plant much closer to the major markets the price is \$87.25 per ton freight equalized. This combination of price differentials and freight equalization permits a high degree of market selectivity.

The purified dentifrice and human food grades of calcium phosphates, which are more costly to produce, command premiums ranging from \$140 to \$170 per ton over feed grades.

The prices of the calcium phosphates, when not in short supply, are determined by competitive processes in the marketplace. Currently, however, they are in short supply and would rise if there were no controls.

Because of the low margins of profit currently generated by STPP, it can be expected that producers will attempt to pass on any cost increases that result from water pollution control measures. This is also probable with feed grade dicalcium phosphate, but the results will be somewhat dependent upon the supply-demand situation at the time of increased costs.

SECTION III

ECONOMIC IMPACT ANALYSIS

I. INTRODUCTION

This section assesses the economic impact of water pollution control costs on the production of the following nonfertilizer phosphate products:

Phosphorus
Phosphoric Acid produced from phosphorus
Phosphorus Pentoxide
Phosphorus Trichloride
Phosphorus Oxychloride
Phosphorus Pentasulfide
Sodium Tripolyphosphate
Calcium Phosphates (except defluorinated phosphate and fertilizer phosphate).

As requested by EPA, this impact analysis is confined to those water pollution control costs submitted to EPA in Supplement A of a report entitled "Cost Information for the Water-borne Wastes in the Nonfertilizer Phosphorus Chemicals Industry" prepared by General Technologies Corporation, referred to as the effluent guideline development document. In this report, it was concluded that zero discharge is a reasonable and achievable goal, and it was recommended that this guideline be established for all of the products covered in this report.

At the same time, the effluent guideline development document acknowledges that there may be substantial variation from the costs presented in their report, to achieve zero discharge for individual plants in the industry. That such variations are likely was confirmed in our discussions with some of the major producers of several of the products in this category. If such variations from the costs presented in the effluent guideline development document are significant for individual plants, then the impact of water pollution control costs to achieve discharge may be significantly different than those presented in this analysis.

Because we were unable to quantify the variations for individual plants, we did confine ourselves, as requested by EPA, to assessing the impact of the costs presented in the effluent guideline development document. It was not within the scope of our assignment to evaluate or confirm the validity of the technical and economic information presented in this document.

II. IMPACT ANALYSIS

A. WATER POLLUTION CONTROL COSTS

The effluent guideline development document states that zero water discharge is either being currently achieved, or could be achieved with little difficulty, in exemplary plants now operating in each product category, and therefore have recommended that this be established as the pollution guideline. The technology proposed by the effluent guideline development document for each product segment, and the estimated costs, are presented below.

1. Phosphorus

Three companies are producing phosphorus in separate locations in Florida with a total of four furnaces, three companies are operating in Tennessee with a total of ten furnaces, and three companies are operating in Idaho and Montana with a total of nine furnaces. In addition the TVA operates three furnaces in Alabama.

There is at least one existing plant that is reported in the effluent guideline development document to achieve zero discharge by using complete recycle of phossy water, evaporation of some process water, lime treatment and sedimentation of remaining process water prior to discharge. Other plants were estimated to be able to achieve 100% recycle of process waste water back to the head end of the plant by installing pumps, piping, and appropriate controls.

The cost of achieving zero discharge through installation of the equipment described above is estimated in the effluent guideline development document to be \$4.60 per ton of phosphorus.

2. Furnace Phosphoric Acid

There are an estimated 21 plants producing furnace phosphoric acid from phosphorus, operated by six companies, and the TVA. Many of these have associated with them units for the production of various sodium and potassium phosphates. A number of these are in urban areas; their location, particularly when associated with the production of sodium tripolyphosphate, has been dictated by proximity to major detergent factories.

The measures necessary to achieve zero discharge at furnace acid plants, according to the effluent guideline development document, are generally associated with improved housekeeping and maintenance. Costs included construction of dikes and dams around pipes, valves, tanks, etc., the provision of sumps and sump pumps, and treatment with lime. The resultant sludge is used for landfill.

In the effluent guideline development document, it is estimated that the cost of achieving zero discharge in furnace acid plants is \$0.65 per ton of 75% phosphoric acid.

3. Anhydrous Derivatives of Elemental Phosphorus

The four derivatives comprising this segment are phosphorus oxychloride, phosphorus pentasulfide, phosphorus pentoxide, and phosphorus trichloride. All four are produced under anhydrous conditions and the water pollution aspects are limited to disposal of water used for wet scrubbing of air emissions. However, the disposal of such water is critical because there is no remedy available through return of this water to the reaction process because of the anhydrous conditions of manufacture.

The primary plant sites are Nitro, West Virginia; Niagara Falls, New York; Sauget, Illinois; Anniston, Alabama; Charleston, South Carolina; Morrisville, Pennsylvania; Mt. Pleasant, Tennessee; Nashville, Tennessee; and Cold Creek, Alabama. In general these are large multiproduct, integrated operations producing dozens of individual chemical products of which the volume represented by the derivatives of elemental phosphorus may be only a portion of the chemical output of the site.

In general the process water used for wet scrubbing of air emissions is commingled with plant effluent water and not treated separately to remove dissolved or particulate impurities. In some cases water from the wet scrubbing may be used as process water in other processes where such opportunities are available but this is not a practical general solution.

In the case of the four derivatives of elemental phosphorus, the effluent guideline development document recommends the attainment of zero discharge via (1) concentration of impurities through reuse of wet scrubbing effluent by return to the wet scrubbing process; (2) lime treatment of concentrated effluent; (3) settling tanks; and (4) land fill of sludge.

The costs presented in the effluent guideline development document for total treatment of effluent to achieve zero discharge are as follows, on the basis of \$/per ton of product manufactured.

| Zero Discharge Cost |
|---------------------|
| \$1.25/ton |
| 1.70/ton |
| 1.40/ton |
| 1.40/ton |
| |

4. Derivatives of Phosphoric Acid

This segment is restricted to sodium tripolyphosphate (STPP) and those calcium phosphates used industrially or in the manufacture of animal feeds. The latter category of calcium phosphates, i.e., those used for the manufacture of animal feeds, accounts for more than 90% of the calcium phosphates included in the segment. Excluded from the segment is fertilizer consumption of calcium phosphate.

The primary plant sites are indicated in Table 20. The STPP locations and several of the calcium phosphate locations are large multiproduct integrated operations producing a number of individual chemical products. This is less typical of the feed grade calcium phosphate plants which are sited for either proximity to wet process acid or the animal feed compounders representing the market.

TABLE 20

PLANT LOCATION SITES - PHOSPHORIC ACID DERIVATIVES

Carteret, New Jersey Green River, Wyoming Newark, California Lawrence, Kansas Fernald, Ohio Augusta, Georgia Kearny, New Jersey Long Beach, California Trenton, Michigan Carondelet, Missouri Dallas, Texas Jeffersonville, Indiana Joliet, Illinois

Chicago, Illinois

Morrisville, Pennsylvania

STPP

Weeping Water, * Nebraska Alden, Iowa Hannibal, * Missouri Plant City, Florida Peabody, Massachusetts Bonnie, Florida Carondelet, Missouri Davenport, Iowa White Springs, Florida Chicago Heights, Illinois Nashville, Tennessee

Calcium Phosphates

To a considerable degree the water used for wet scrubbing of dust at various points in the process is returned to process. Where such return to process is not readily accommodated, lime precipitation and clarification are required. The purified grades of calcium phosphates in particular require large volumes of process water. Special problems relate to the disposal of water removed from anhydrous calcium phosphate and the disposal of fluosilicates from those calcium phosphate plants using wet process acid which has not been defluorinated.

^{*}Location of more than one plant.

In the case of the derivatives of phosphoric acid only the calcium phosphates have costs associated with the achievement of zero discharge as reported in the effluent guideline development document. This asserts that dry dust collection filters constitute an investment which obviates water pollution in the case of STPP and the investment per se is compensated for by savings in product recovery.

In the case of dicalcium phosphate manufacture, the costs associated with zero discharge are generally related to (1) lime treatment, (2) settling or filtration, (3) recycle of clarified water to the process, and (4) land fill of sludge or filter cake.

The costs presented in the effluent guideline development document for total treatment of effluent to achieve zero discharge are as follows on the basis of dollars per ton of product manufactured.

| Product | Zero Discharge Cost |
|----------------------------------|---------------------|
| | (\$/ton) |
| STPP | _ |
| Dicalcium phosphate - Feed Grade | 1.40 |
| Dicalcium Phosphate - Food Grade | 1.50 |

B. IMPACT ON PRICES

We have summarized in Table 21 the increases in prices that would result from the costs of achieving zero discharge that are presented in the effluent guideline development document. It should be noted that we have included not only the costs of water pollution control for individual products, but also the increases in the costs of the raw materials covered in this segment which are used for the production of derivatives, arising from the same water pollution control considerations. For example, the overall increase in prices for Food Grade calcium phosphate would result not only from the cost of water pollution control in the dicalcium phosphate plant, but also the increase in the cost of furnace grade phosphoric acid arising from water pollution control considerations in that plant, and also the increase in cost of phosphorus used to make the furnace acid, arising from water pollution control considerations plant.

The price increases that would result from passing on the cost of achieving zero discharge, as presented in the effluent guideline development document, are of such small magnitude that we do not believe there will be any significant impact on profitability arising from these increases. The maximum increase as a percent of current selling price was 1.6% for Feed Grade Dicalcium Phosphate. All other increases were 1.2% of sales price or less. Incidentally, we have used in these calculations the current list prices for the various products, realizing that in some

instances actual sales are being made at somewhat different prices. However, for the purposes of relating the magnitude of the cost increases arising from achieving zero discharge, the use of the list prices is not significantly in error.

PRICE INCREASES RELATED TO GTC PROPOSED COSTS
OF ACHIEVING ZERO DISCHARGE

| Product | Pollution Control Cost (\$/ton) | Raw Material ² Cost Increase (\$/ton) | Total Cost Increase (\$/ton) | Current¹ Price (\$/ton) | Percentage Increase |
|-------------------------|------------------------------------------|--------------------------------------------------|------------------------------------|-------------------------|------------------------|
| Phosphorus | 4.60 | _ | 4.60 | 380 | 1.2 |
| Furnace Acid | 0.65 | 1.10 | 1.75 | 168 | 1.0 |
| Phosphorus Pentoxide | 1.40 | 1.09 | 2.49 | 400 | 0.6 |
| Phosphorus Trichloride | 1.40 | 1.09 | 2.49 | 220 | 1.1 |
| Phosphorus Oxychloride | 1.25 | 1.83 | 3.08 | 245 | 1.2 |
| Phosphorus Pentasulfide | 1.70 | 1.32 | 3.02 | 267 | 1.1 |
| STPP | _ | 1.90 | 1.90 | 162 | 1.2 |
| Feed-grade Dical | 1.40 | _ | 1.40 | 87 | 1.6 |
| Food-grade Dical | 1.50 | 1.35 | 2.85 | 257 | 1.1 |

^{1.} Prices based on Chemical Marketing Reporter, 7/23/73.

2. Based on following usages:

| 0.24 tons phos/ton acid | 1.09 tons acid/ton STPP |
|--------------------------------|-------------------------------------|
| 0.24 tons phos/ton pentoxide | 0.77 tons acid/ton food grade dical |
| 0.24 tons phos/ton trichloride | 0.29 tons phos/ton pentasulfide |

0.19 tons pentoxide + 0.55 tons trichloride/ton oxychloride.

Our conclusion that the cost increases of the magnitude indicated in the effluent guideline development document would be of insignificant consequence, is further supported by the nature of the markets for the products in question. The uses of the products in this segment are such that there is little if any ability to substitute other products, should price increases so suggest. Because of the specific requirements for the individual products in this segment, it is almost certain that the price increases, particularly of the small magnitude which apparently would result, would be passed on to the ultimate consumer.

The one possible exception is Feed Grade Dicalcium Phosphate, where there is a possibility of substituting other phosphate materials without too much difficulty, if the price increase in the dicalcium phosphate were substantial. Such materials as defluorinated phosphate rock could be used although there are specific advantages which the dicalcium phosphate does have for certain feed

formulations. Even in the case of this product, however, the price increase is so small that we do not foresee any impact of a major nature on profitability.

If the premise is accepted that the costs of achieving zero discharge as presented in the effluent guideline development document would have a negligible effect on profitability, then it follows that no production curtailments or plant closings would be foreseen for any of these products nor would there be restrictions on industry growth, as a direct result of the cost increases for achieving zero discharge.

No significant impact would then be expected on employment in the plant producing these products or on the communities in which they are located, as a result of the cost increases to achieve zero discharge.

III. LIMITS OF THE ANALYSIS

The cost increases for achieving zero discharge, as presented in the effluent guideline development document, have been shown to be relatively small in relation to current sales prices — in no case more than 1.6%. This order of magnitude of cost increase is substantially below the variations which we believe exist among the individual plants producing these products, in their cost of manufacture, and also less than the cyclical variation in prices which may be expected as market conditions change. Therefore the range of error in the conclusions drawn from the cost presented is believed to be small and would be overshadowed by uncertainties in the estimates of the cost of manufacturing, and in the variation in manufacturing costs from plant to plant.

The critical question concerning these conclusions is of course the extent to which the costs presented in the effluent guideline development document can be realistically used as a basis for estimating the costs that will be incurred by specific individual plants within the industry. In several cases, producers felt that the costs presented in the effluent guideline development document were unrealistically low, and also that in certain cases, the technology to achieve zero discharge was of questionable validity. Preliminary contacts with major producers of several of the products examined have confirmed that major variations do occur among individual plants regarding the applicability of both the technology, and the cost estimates as presented in the effluent guideline development document. It was not within the scope of our report to evaluate or confirm the validity of either the technology or of the estimates of the investment and operating costs to achieve zero discharge, which were presented in the effluent guideline development document.

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| An initial a upon certain pr | nalysis of the economic oducts in the industrial | l phosphate indu | osed water effluent guideline ustry. This analysis was bas |

An initial analysis of the economic impact of proposed water effluent guidelines upon certain products in the industrial phosphate industry. This analysis was based on abatement cost data supplied by the EPA. The products covered included phosphorous, phosphoric acid produced from phosphorous, and anhydrous phosphorous derivatives, and certain derivatives of phosphoric acid but not including fertilizers.

The effluent guideline development document supplying the abatement costs used in this analysis indicated that zero discharge was a practical goal and that the cost of achieving zero discharge did not exceed 1.6% of the selling price of any of the products studied. On the basis of these costs, it was concluded that there would be no significant economic impact on the products studied.

17. Key Words and Document Analysis. 17a. Descriptors

Economic Analysis
Effluent Guidelines
Industrial Phosphates
Phosphorous
Phosphoric Acid
Industrial Phosphate Industry

17b. Identifiers/Open-Ended Terms

1244

| 8. Availability Statement Limited availability through U.S. Environmenta | 1 Re | ecurity Class (This eport) UNCLASSILILD | 21. No. of Pages 55 |
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Mobil Chemical Company

HOLAST CHO STREET REW YORK, REW YORK 1007

October 6, 1973

EPA Information Center Environmental Protection Agency Washington, D.C. 20460

Attention: Mr. Philip B. Wisman

Gentlemen:

We are pleased to take this opportunity to comment on Proposed Effluent Limitations Guidelines, New Source Standards and Pretreatment Standards for the Phosphate Manufacturing Point Source Category, published in the Federal Register on September 7, 1973, (Vol. 38, no. 173, CFB Part 422).

The requiring of zero discharge by 1977 appears to go beyond the intent of Congress which targeted zero discharge as a goal for 1985. The intent we believe was to establish standards representing the range of the best practicable performance by plants of different sizes, ages, and processes. The contractor chose the single best plant which in our judgment doesn't follow the BPT guidelines which should reflect the range of exemplary performances.

Comments on the three sub-categories are as follows:

Phosphorus Production: Our information indicates that only one plant is capable of achieving zero discharge and is unable to do so when it is raining. Although other plants have achieved high control and low quantities of discharge they have not achieved zero discharge.

Accordingly, we agree with the limits proposed by the Sager Committee:

| P4: | 0 | |
|------|-------------------------|------|
| PO4: | 0.2 to 0.4 lbs. per ton | |
| F: | 0.2 to 0.3 lbs. per ton | 1246 |
| TSS: | 0.5 to 1.0 lbs. per ton | |

Phosphorus Consuming: We currently manufacture only phosphoric acid and phosphorus trichloride in this subcategory. We would anticipate difficulty achieving zero discharge for phosphoric acid unless permitted to discharge spills, leaks and contaminated cooling water after adequate treatment. Recycling of this material would conflict with

production of a food grade product.

Establishment of dissolved solids limits for PCL₃ is improper based on the fact that the best practicable technology for control of total dissolved solids is not clearly established.

Phosphate: Zero discharge has been recommended for sodium tripolyphosphate. We have not achieved zero discharge and again suggest the application of the limits proposed by the Sager Committee.

The subject proposal precludes the public treatment of seven zero discharge products which again we believe is contrary to encouraging public treatment. BPT limits recommended by the Sager Committee would clarify this regarding existing plants.

Time has not permitted us to make a study of the cost data submitted by the contractor.

In summary, we feel that the limits proposed by the Sager Committee, which represents a range of exemplary performance, should be adopted.

Very truly yours,

J. V. Agnes

Manager, Environmental Control

FMC Corporation

10 OCT 1973

Chemical Group Headquarters 633 Third Avenue New York New York 10017 (212) 687 7400 Phosphetes 22

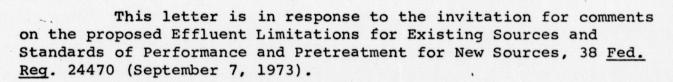
4FMC

October 9, 1973

Environmental Protection Agency Waterside Mall Washington, D.C. 20460

Attention: Mr. Philip B. Wisman

Dear Sir:



The Manufacturing Chemists Association has submitted comments pointing out the basic problems with the proposed regulations and suggesting, where feasible, alternatives. FMC Corporation concurs in and supports the comments of the Manufacturing Chemists Association.

The Effluent Standards and Water Quality Information Advisory Committee in its September 25, 1973, report to the Administrator demonstrated the Agency's current methodology to be unscientific. On August 31, 1973, the Committee submitted specific recommendations to the Acting Administrator on the phosphate industry. FMC commends the alternative methodology proposed by the Committee.

This letter is intended to supplement MCA's comments and complement the Advisory Committee's report by pointing out an additional defect in the Agency's development of effluent guidelines -- the lack of a usable administrative record against which the regulations can be judged.

Recent litigation has firmly established the principle that the Agency must present a record which allows the Court to

Environmental Protection Agency Page Two October 9, 1973

assess whether the Agency's "decisions and reasons therefore are themselves reasoned." Essex Chem. Corp. v. Ruckelshaus, D.C. Cir., September 10, 1973, at 12. In FMC's judgment, this principle applies equally to the benefit of affected industries and the public.

The Agency, at least by the time it proposes regulations, should make available a record which demonstrates the Agency's reasoning and allows correlation of the data base compiled by it to the Agency's conclusions on all material points. Without adherence to this principle, informed comment on the proposal is virtually impossible.

In an effort to assess the content and adequacy of the Administrative record supporting the proposed regulation for the phosphate industry, FMC Corporation, on September 13, 1973, requested, through its counsel, an opportunity to review and duplicate the administrative record supporting the proposed regulations. Appended hereto is a complete list of all documents produced or reviewed in response to that request and correspondence relating thereto.

Included in the list are computer printout sheets of Refuse Act permit applications. It was not feasible to review these documents because they were produced for review at the Public Information Center mid-afternoon Friday, October 5; the permit applications were mingled with applications of a different industry; there were no citations in "Development Document" of which applications were relied upon; and we were unable to determine whether the applications reflect current data.

FMC Corporation believes that additional documents on industry-wide economic impact may be in the possession of the Office of Planning and Evaluation. In response to the letter of September 24, 1973, counsel was advised such documents would relate solely to the August 1973 "Economic Analysis" (the economic impact of the proposals on the industry as a whole) and not to abatement technology or costs. Therefore, since the validity of the "Economic Analysis" hinges on abatement cost data prepared by the Effluent Guidelines Division and its contractor, FMC Corporation considered review of documents in the possession of the Office of Planning and Evaluation as unlikely to result in information of value for purposes of comments on the proposed regulations.

Environmental Protection Agency Page Three October 9, 1973

The documents produced (plus those in the possession of the Office of Planning and Evaluation and comments received in response to the proposed regulations) constitute the entire administrative record against which the effluent guidelines, standards of performance, and new source pretreatment standards must be judged. The Agency's regulations (40 C.F.R. Part 2) provide a mechanism for withholding documents not subject to disclosure and for notifying the requesting party of such a determination. A portion of one document was identified by the Agency and production declined because it had been designated as confidential by the submitting company. No other documents were specifically identified as being withheld on the ground that they constituted trade secrets, intra-agency memoranda relating to policy, or otherwise were not subject to disclosure.

The inadequacies of the administrative record for the phosphate industry are patent. There are no documents which attempt to correlate the conclusions stated in the draft "Development Document" to data obtained by the Agency or its contractor. Indeed, the draft "Development Document" only rarely employs the rudimentary mechanism of specific citations to the references listed therein as required by Portland Cement Ass'n v. Ruckelshaus, D.C. Cir., June 29, 1973, slip op. at 48 and 52.

As a consequence, it is impossible to evaluate and prepare meaningful comments on the Agency's basis for the proposed guidelines. FMC notes that this is not a problem just recently discovered. At an early public meeting of the Effluent Standards and Water Quality Information Advisory Committee it was suggested that the Committee could benefit from having available to it in an organized manner basic data compiled by the Agency; to FMC's knowledge, such information has never been made available. Industry representatives, on a number of occasions, have requested, but never received, detailed information on the basis of Agency

In addition to the documents listed in the appendix, a binder described as "Back-Up Information for Interim Effluent Guidances for the Inorganic Chemical Industry" was provided. That set of documents is not a part of the administrative record in that it consists of mere conclusions reached by the Agency outside of required procedures and without reference to necessary substantive criteria established by the Federal Water Pollution Control Act () Amendments of 1972 (P.L. 92-500).

Environmental Protection Agency Page Four October 9, 1973

proposals. Other commentators have discussed the difficulty of testing the Agency's reasoning. <u>E.g.</u>, Items C-4, D-14, E-1, E-3, F-3, and F-15 as listed in the Appendix to this letter.

It is impossible to be exhaustive as to the material questions that cannot be answered by reference to the administrative record. However, FMC hopes that a few illustrative examples may assist the Agency in improving the records by which its regulations will be judged. This, in FMC's view, is imperative if the objectives of the 1972 Act are to be carried out without unnecessary delay, confusion, and controversy.

The Agency has based the proposed regulations on combinations of exemplary practices at different plants and by technology transfer for those subcategories in which no plant meets the proposed standard. This approach has been criticized (Item F-14) with substantial justification in the 1972 Act (118 Cong. Rec. S16873; S. Rep. No. 92-414, at page 50). The only portions of the administrative record which might provide the factual basis for the conclusions reached in Development Document on exemplary plants and technology transfer are Items C-1 through C-3, C-5 through C-13, and F-18.

Those documents, many handwritten, are difficult and sometimes impossible to decipher. The raw data lack such elementary validating information as sampling and analytical techniques, operating and meteorological conditions at the time of sampling, etc. Item H-2. Only rarely can the data, assuming their validity, be correlated to data and conclusions in the "Development Document."

When they can be correlated, the data raise more questions about the factual basis for the proposed regulations than they answer. For example, there are no data prepared by EPA or its contractor for one exemplary plant (TVA) despite the fact that it has been repeatedly pointed out that EPA's assessment of performance of that plant is erroneous (Items C-4, D-2, D-7, and E-1). For another, the data (C-6) demonstrate process effluent from overflow during wet conditions; yet, there are no data indicating the conditions under which this occurs, quantity or quality of process effluent involved, methods of preventing process discharges, the cost thereof, or applicability to other plants.

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Environmental Protection Agency Page Five October 9, 1973

The TDS limits for PCl₃ and POCl₃ plants raise an equally serious problem. FMC has been unable to proceed logically from the data in Items C and F-18 to the BPCTCA limits. With respect to the BAT and the standards of performance, the only factual information relates to the lack of technology for TDS removal (e.g., F-16). The "Development Document" basis for technology transfer (refrigerated condensors) is nowhere referred to in the record as used or contemplated for use in PCl₃ or POCl₃ plants.

FMC would have thought that engineering judgment would lead to evaluation of such potential technology in the context of individual PCl₃ and POCl₃ plants visited; there are no such data in the record. In the absence of data "demonstrating" the technology for such plants (and in light of the high energy demand of the technology), FMC believes that the standard should not be adopted for Level II or the new source standards, bearing in mind that these standards may be revised as new data warrants.

The Development Document contains a fifteen-page discussion of the cost of pollution abatement for the industry. The record is a virtual blank on costs.

There are no citations in the Development Document to supporting documentation in the record and only a few isolated references to cost in the record, many of which, as pointed out in MCA's comments, contradict the Development Document. Basically for that reason, it is impossible to determine in a meaningful manner how costs summarized in Table 18 of the Development Document were calculated.

In addition, the Development Document is replete with vague recommendations on housekeeping, minimization of storm water runoff, and other practices that are not part of the no-process waste standard (or the finite BPCTCA limit for PCl3 and POCl3 plants) and deferred abatement problems such as boiler and cooling water blowdown, percolation to ground water, and solid waste disposal for which no cost is estimated but which may involve substantial costs. For example, FMC estimates that rigorous fail-safe housekeeping measures at its STPP plants to minimize further already minimal non-process sources of pollutants (runoff and minor leaks and spills) could entail capital costs nearly 50 times the highest capital cost figure in the Development Document.

Environmental Protection Agency Page Six October 9, 1973

This, in FMC's judgment, is a major defect in the administrative record, as is the failure to include in the economic impact analysis the cumulative impact of air, water, solid waste, OSHA, and other environmental requirements. This practice of overlooking or deferring assessment of substantial problems was the basis for remand in Essex Chem. Corp. v. Ruckelshaus, D.C. Cir., September 10, 1973, at 20-23.

Very truly yours,

Neil C. Elpheck Neil C. Elphick

Director

Environmental Planning Department

10 OCT 1973 Phosphetis 22



MANUFACTURING CHEMISTS ASSOCIATION

1825 CONNECTICUT AVENUE, N. W. . WASHINGTON, D. C. 20009 € (202) 483-6126

WILLIAM J. DRIVER
PRESIDENT

October 9, 1973

EPA Information Center
U. S. Environmental Protection Agency
Washington, D. C. 20460

Attention: Mr. Philip B. Wisman

Subject: Proposed Effluent Limitations Guidelines for Existing Sources and Standards of Performance and Pretreatment Standards for New Sources - Phosphate Manufacturing Point Source Category - (40 CFR Part 422)

Dear Sirs:

The following comments and appended Technical Assessment are submitted on behalf of the Manufacturing Chemists Association (MCA), a non-profit trade association with 170 United States member companies representing more than 90 percent of the production capacity of basic industrial chemicals within this country. As manufacturers and handlers of the chemicals in question, our members have a direct and critical interest in the proposed rules published in the September 7, 1973, FEDERAL REGISTER.

Our reaction to the proposal is one of serious concern. While the preamble recognizes some issues previously raised by interested parties, some of the more critical problems have been neither recognized nor addressed and few of the issues have been dealt with to any essential degree. We conclude that:

Zero discharge does not constitute best practicable control technology, in that such a standard would not describe the range of exemplary performance currently practiced.

- The proposed guidelines conflict with pretreatment standards and essentially prohibit any continued or future industrial participation in joint treatment facilities.
- The economic impact study supporting the proposed guidelines is seriously understated.

Considering all factors, we recommend that the final regulations not be promulgated in the form proposed. We urge EPA instead adopt the specific August 31, 1973 recommendation of the Effluent Standards and Water Quality Information Advisory Committee and provide for effluent limitations based on appropriate recognition of waste load, size, age, and type of facility and geographic factors. The subsequent September 25, 1973 recommendations of ES&WQIAC further support the need to recognize such factors.

Sincerely,

d.

1. Effluent Standards and Water Quality Information Advisory Committee August 31,1973 Action Memorandum on Proposed Effluent Limitations Guidelines, Standards of Performance, Pretreatment Standards for New Sources and Information on Alternative Treatment Methods for the Phosphorus Derived Chemicals Segment of the Phosphate Manufacturing Point Source Category.

 Effluent Standards and Water Quality Information Advisory Committee Evaluation of Current Methods for Establishing Effluent Limitations for Industrial Point Source Discharge

dated September 25, 1973

TECHNICAL ASSESSMENT

of

PROPOSED GUIDELINES AND STANDARDS OF PERFORMANCE for PHOSPHATE MANUFACTURING POINT SOURCE CATEGORY

Interest in the technical development of guidelines for EPA's effluent limitations program is relatively longstanding. The first formal comments specific to phosphate were presented at the Effluent Guidelines and Standards Division's "Inorganic Chemicals Industry Effluent Limitation Guidance Regional Industrial Seminar" on November 16, 1972. On August 1, 1973, in a letter to Mr. Allen Cywin concerning the June 1973 draft development document on the non-fertilizer phosphorus chemicals industry, we transmitted technical comments and included those of FMC Corporation specific to phosphorus chemicals. Technical experts from various chemical manufacturing companies have also commented formally and informally to EPA, General Technologies, Inc., and the Effluent Standards and Water Quality Information Advisory Committee.

It is not apparent that EPA has given any consideration to these comments and recommendations. For this reason, a number of the more substantive points are herein reiterated.

Zero Process Discharge

Public Law 92-500 establishes zero discharge as

a goal for 1985. Requiring the actual achievement of that goal by 1977 appears to go far beyond the intent of Congress.

Legislative history relative to effluent standards indicates that Congress intended that by 1977 the applicable standards represent the range of best practicable existing performance by plants of various sizes, ages, and processes. According to the contractor's report, exemplary operations which achieve 95 - 100 percent removal of pollutants would be made obsolete by the proposed standards. These operators have, in good faith, invested in water quality control schemes using advanced, end-point treatment.

BPT guidelines should constitute a range of performance which encompasses "the range of exemplary performance" - not just the best single plant or, in the case of several products, the best combination of technology (undemonstrated) transferred from other products.

Considering the three sub-categories:

(1) Phosphorus: The zero process discharge guideline is based on just one of the ten U. S. manufacturing plants. The operator of this plant states zero discharge can be maintained only when it is not raining.

1203

Senator Muskie's remarks during Senate consideration of P.L. 92-500 Conference Report.

^{2.} P. 126, EPA 440/1-73/006 Development Document RE: Plants 028 & 159.

^{3.} P. 134, EPA 440/1-73/006 Development Document RE: Plant 006

Authority's Phosphate Demonstration Center in Alabama as achieving zero discharge of process waters other than phossy water. Both TVA and the Effluent Standards and Water Quality Information Advisory Committee have stated that this claim is not factual.

The Report further states that two plants achieve "very high (97 to 99+%) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents."²

Producers concur in the numerical limits recommended

by the Effluent Standards and Water Quality Information Advisory

Committee for promulgation as guidelines representative of the

"range of exemplary performance."

| These limits are: | Elemental Phosphorus | 0 |
|-------------------|------------------------------|-------------------|
| | Suspended Solids | 0.5 - 1.0 lb/ton |
| | Phosphate (PO ₄) | 0.2 - 0.4 lb/ton |
| | Fluoride (F) | 0.2 - 0.3 lb/ton |

(2) Direct Phosphorus Derivatives: This sub-category includes phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. Zero process discharge is recommended for the first three, and limits are proposed for the last two.

Zero process discharge represents BPT for phosphoric acid if discharge of leaks, spills, and contaminated cooling water

is allowed after suitable treatment. Recovered materials cannot, however, be recycled back into the process without violating quality requirements for hi-purity (frequently food-grade) products.

For the remaining products, it is stated that the recommended levels <u>have</u> not been achieved by any plant. The validity of the assumed BPT basis and the practicality of installing undemonstrated technology as a NPDES permit condition is basis for concern.

It would be more practical for a qualified group such as the Effluent Standards and Water Quality Information Advisory Committee to solicit proposals as to what would constitute reasonable BPT and recommend defensible numerical limits rather than to adopt synthesized zero discharge rationale assembled by the contractor. The dissolved solids limits proposed for phosphorus trichloride and oxychloride appear inappropriate in the light of the recognized lack of practicable technology for TDS control.

(3) Phosphates: This sub-category includes sodium tripolyphosphate (STPP) and both food and feed-grade dicalcium phosphate. Zero process discharge is recommended for both.

Zero discharge is probably BPT for non-food-grade, singleproduct STPP plants. Where food-grade restrictions apply and/or other salts (such as calcium, ammonium, potassium, or sodium phosphates) are manufactured, however, zero process discharge technology is not applicable.

The Federal Register and the Development Document state that the entire industry (fifteen plants) has already achieved zero process discharge, however, only two plants are known to have demonstrated this ability. Thus, the technology basis is grossly overstated, and the economic costs grossly understated. The conclusion that zero discharge is justified on the basis of economics is not factual.

The food-grade dicalcium phosphate technology is undemonstrated and the contractor has suggested a combination of steps (conversion from wet to dry dust collection, lime treatment/vacuum filtration, and polymeric clariflocculation) which are untried.

Effluent Standards and Water Quality Information Advisory Committee has suggested a range of numerical limits which producers feel are technologically reasonable for the phosphate sub-category. These limits would allow use of best practicable end-point treatment rather than imposing total process recycle as the only technology which may be applied. This would be consistent with EPA's long-stated position of not dictating specific technology or how limitations are achieved.

Pretreatment Standards

In CFR 40 Part 128 it is proposed that any pollutants other than BOD, suspended solids, fecal coliform, and pH, are by definition incompatible pollutants and must be treated (pre-treatment and public treatment) to BPT levels as defined in the 304(b) Effluent Guidelines.

For the seven recommended zero discharge products, public treatment would be <u>forbidden</u> in that they involve waste parameters other than the four defined as compatible (i.e., dissolved solids, COD, color, etc.). This appears contrary to the intent of Congress to encourage public treatment.

Adoption of the numerical BPT limits recommended by the Effluent Standards and Water Quality Information Advisory Committee would resolve this conflict for existing plants.

The zero discharge new source pretreatment standard should receive similar consideration. Recently released "Pretreatment Guidelines" suggest "no pretreatment required" for STPP.

Treatment Costs

The contractor has estimated the total industry will spend \$9.2 million to achieve the recommended discharge levels. One manufacturer alone, representing only seven of the eighty plants involved, might spend this amount!

The compliance cost estimate for "representative plants" in six of the eight product categories is in the \$0 - \$50 million range. These facilities generally involve separation of products and non-contact water systems, surge tanks, pumps, lime treatment facilities (lime unloading, storage, slaking, slurry surge, pumps, and lines), clariflocculators, settling ponds, polymer feed systems, vacuum filtration, effluent surge, and recycle pumps and lines. The \$500,000 estimate for phosphorus plants represents a simplistic scheme of pumping the representative plant's effluent (Plant 028) back to the intake. This "system" would not only be unworkable, but the use of a single exemplary plant as representative of the entire industry is improper. This plant estimates zero process discharge compliance cost at \$2.4 million.

A. D. Little's position is that the economic impact study, no matter how detailed, is no better than the compliance data provided them by EPA. It would not appear that the economic impact on this industry has been properly characterized.

Sie Mar Circulturi Company

October 5, 1973

Mr. Allen Cywin
Director, Effluent Guidelines Division
Office of Air & Water Program
Environmental Protection Agency
Washington, D.C. 20460

Dear Mr. Cywin: .

We wish to comment on the EPA-proposed guidelines for the non-fertilizer phosphates industry.

We are particularly concerned about the recommendations of zero discharge by July 1, 1977. We are unable to obtain zero discharge from any feasible standpoint in our manufacture of the subject products. We attach a copy of our earlier comments on the zero discharge recommendations in the EPA contractor study report. These comments are also valid with respect to the EPA proposed guidelines.

We are in accord with the Manufacturing Chemists Association comments and recommendations regarding these guidelines and urge these be adopted. Although it will take research, time and large expenditures the limits recommended by MCA are probably attainable providing enough land can be found for disposal of the thousands of tons of solid waste which will result from using lime for chemical treatment of effluents, and providing the nation does not exhaust its lime-producing capacity.

We are deeply concerned about the grossly erroncous and misleading cost information contained in the contractor's development document upon which the proposed guidelines are based. For example EPA 440/1-73/006 page 119 gives estimates of installed costs of stainless-steel single effect evaporators. Stauffer's engineers estimate costs 4-5 times the costs given by EPA (see Table I attached).

Another example is the BPA contractor estimate that the 79

plants involved would have to spend only 9.2 million to achieve the proposed guidelines. An EFA news 1.3 widely contributed, (wall Street downal 9/4/73, 642.) these highly erroneous figures. One producer estimates would cont his company alone 10 million dollars to 1.2 guidelines. Another company estimates that 9.2 million dollars would not even buy the engineering work near 1.3 the 79 plants for meeting the proposed guidelines.

Please do not promulgate guidelines based on such minimum tron.
Sincerely,

Edgar L. Conant Manager Environmental Control ELC:ak att.

Mooker Industrial chemicals COLUMBIA, TENNESSEE 38401, PHONE (615) 388-67 September 28, 1973 Mr. Phillip B. Wiseman Environmental Protection Agency Washington, D. C. 20460 Dear Mr. Wiseman: • Re: (40 CFR Part 422) Phosphate Manufacturing Federal Register Vol. 38, No. 173, Part 11 Friday, September 7,-1973 Page 24474 Publication of the proposed rules contains preamble statements on primary issues raised in the technical development of the effluent limitations. Two of the issues (Paragraphs (1) and (5)) relate to the actual and practicable achievements of zero discharge of process waste water pollutants. Paragraph (5) on Page 24474 relates to total recycle and the impact of heavy and prolonged rainfall. Our Columbia, Tennessee plant practices recycle (closed loop system). However, despite our best efforts there are times when "zero discharge" is not attainable, practicularly when we get excessive rainfall. A number of lagoons and large holding ponds have been constructed to accommodate a normal rainfall runoff, and total recycle is practiced. However, during prolonged and heavy rains with runoff from large acreage, these lagoons and ponds fill up; and it is impossible to contain this surplus water. To our knowledge commercial practical technology does not exist for containing and using all runoff in the plant site. The statement that, "plants practicing total recycle will have no difficulty in meeting regulations in arid regions" is meaningless since there is little rainfall and no phosphorus plants in such regions. To our knowledge, there are no phosphorus producers that have achieved "zero discharge" 100% of the time, and it is not correct to state that, "it may be more difficult to practice total recycle in a humid region than in a dry region, established sound procedures for lagoon design location and for control of rainfall runoff are among the factors that make the regulation practicable." EPA treatment of this issue is apparently based on information General Technologies, Inc. obtained at our Columbia, Tennessee plant; and we wish it noted that on several occasions we raised this point with General Technologies, Inc. noting the impracticability of containing all storm runoff. Holding ponds (lagoons) in the Tennessee area are constructed according to the best practicable technology. To make these ponds deeper would createmore problems. All of these ponds are constructed in hilly country. Drainage from the surrounding area flows into and fills these ponds during heavy rainfalls. Due to geographic location and topography of the surrounding countryside, it is impractical to consider diking of the ponds to prevent intermingling of rainfall runoff with process water. 1271 HOOKER CHIMICAL CORPORATION LITTY OF OCCIPINATE PERFOLEUM CORPORATION

I would also point out that when excessive and prolonged rainfall conditions exist, surface streams are usually in flood stage and minor contaminants resulting from pond effluent discharges have no detrimental effect on the receiving streams at these times.

Since this problem occurs not only in phosphorus and phosphorus product plants, we suggest a section be added to this as well as all other regulations calling for "no discharge of process waste water pollutants" to exempt the discharge of storm runoff waters from plant sites and surrounding areas which might contain trivial quantities of pollutants normally found on surfaces in manufacturing locations.

In addition provisions should be made for discharge of contaminated water containing limited levels of contamination from ponds in humid areas where a net positive water balance exists when natural and process inputs are compared with evaporation rates.

These actual experience factors should be considered in your final determination of "zero discharge" 100% of the time in this industry category. We would welcome the opportunity to discuss this matter further with EPA.

Sincerely yours,

HOOKER CHEMICAL CORPORATION

E. F. Smith, Manager

Environmental Monitoring

EFS/pr

cc: Mr. John Quarles
Acting Administrator
United States, EPA
Washington, D. C. 20460

Mr. Allen Cywin, Director Effluent Guidelines and Standards Division Office of Water Programs, EPA Washington, D. C. 20460

Dr. Martha Sager, Chairman Effluent Standards and Water Quality Information Advisory Committee, EPA Washington, D. C. 20460 Llonsanto

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MORSANTO INDUSTRIAL CHEMICALS CO.

800 N. Liedburgh Boulevard St. Louis, Missouri 63166 Phone: (314-694-2008

October 2, 1973



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EPA Information Center (3) Environmental Protection Agency Washington, D. C. 20460

Attention: Mr. Philip B. Wisman

Subject: 40 CFR 422 - Propo

40 CFR 422 - Proposed Phosphate Manufacturing

Effluent Standards

Gentlemen:

Monsanto Industrial Chemicals Company is a major participant in the Non-Fertilizer Phosphate Chemicals industry and considers the promulgation of fair, effective effluent standards of utmost importance. Accordingly, we have worked very actively with the contractor during four plant visits, provided extensive input to the Effluent Standards Advisory Committee (ESWQIAC), contributed sensitive financial data to the economic impact study, and commented on several occasions directly to the Effluent Guidelines Division. We are, quite frankly, very disappointed with the lack of response to this past input and trust that these comments will receive sincere consideration. We have not burdened this submission with copies of past inputs which we know to be a part of the public record as constituted in your office.

We have attached, however, two recent inputs to the Agency which are relevant. Attachment A is a copy of a statement made to the Effluent Guidelines Advisory Committee on September 20 which summarizes our comments. Attachment B is a teletype sent to Mr. Quarles on Oct. 2, again highlighting our position. Attachment C is a detailed critique of the Federal Register publication of Sept. 7 and the related Development Document (EPA 440/1-73/006).

As you will determine from these attachments, Monsanto contends:

1) The study upon which this category's zero discharge recommendations are based is fraught with errors.

- 2) Promulgation of zero process discharge as "best practicable control technology currently available" (BPT) is not justified by the Development Document.
- 3) The recommendations of the Effluent Standards Advisory Committee (ESWQIAC) appear to represent BPT in that "the range of current exemplary performance" is reflected.
- 4) Zero discharge standards are incompatible with the proposed 40 CFR 128 pretreatment standards.
- 5) Economic impact data which is offered to support zero discharge is understated by as much as a factor of twenty!

In your final deliberation prior to promulgation, we stand ready to assist in any way possible including documentation of any premise contained herein.

Very truly yours,

C. P. Cunningham

Managing Director,

Vice President

Encs.

MONSANTO INDUSTRIAL CHEMICALS COMPANY ST. LOUIS, MISSOURI

STATEMENT

BY

M. L. MULLINS

MANAGER, ENVIRONMENTAL PROTECTION

BEFORE

THE

SEPTEMBER 20, 1973 PUBLIC MEETING

OF THE

EFFLUENT STANDARDS & WATER QUALITY INFORMATION ADVISORY COMMITTEE

BUILDING #2

CRYSTAL MALL.

ARLINGTON, VIRGINIA

RE:

PROPOSED PHOSPHATE MANUFACTURING EFFLUENT STANDARDS

MONSANTO INDUSTRIAL CHEMICALS COMPANY St. Louis, Mo.

SUMMARY OF COMMENTS

PROPOSED PHOSPHATE MANUFACTURING EFFLUENT LIMITATION GUIDELINES

(40 CFR, Part 422, Federal Register, Vol. 38, No. 173, Sept. 7, 1973)

AND

DEVELOPMENT DOCUMENT

DEVELOPMENT DOCUMENT (EPA 440/1-73/006)

I. SCOPE

The subject guideline proposal deals with elemental phosphorus, phosphorus-consuming processes (phosphoric acid and phosphorus pentoxide, pentasulfide, trichloride and oxychloride) and phosphate processes (sodium tripolyphosphate and calcium phosphate). Put another way, the guidelines cover phosphorus, chemicals made directly from phosphorus and those made from phosphoric acid.

II. EPA PROPOSAL

Zero process discharge guidelines are proposed for all products except for phosphorus trichloride and oxychloride (for which specific numerical limits on TSS [total suspended solids], TDS [total dissolved solids] and pH are given). This means that no water which has contacted process material may be discharged, as opposed to other uncontaminated cooling or utility blowdown streams.

III. MONSANTO PARTICIPATION

Detailed comments on the contractor's draft report were submitted to the ESWQIAC on July 24 and 28 and to EPA Effluent Guidelines Division on July 18 and 20. Also, extensive information was furnished to the contractor during four plant visits (Trenton, Mich.; Columbia, Tenn.; St. Louis, Mo.; and Soda Springs, Idaho) and to the ESWQIAC at its April 30, 1973, workshop at Purdue University.

IV. MONSANTO COMMENTS

The following represents a greatly condensed recap of our comments:

- A "zero process discharge" effluent guideline for the manufacture of elemental phosphorus, sodium tripolyphosphate and food-grade calcium phosphate is not BPT ("Best Practicable 1977 Technology") but probably does constitute BAT ("Best Available 1983 Technology). See details attached.
- 2. Zero discharge for phosphoric acid is BPT.
- 3. Monsanto does not manufacture phosphorus pentoxide and accepts the recommended limits on phosphorus trichloride and oxychloride. We are skeptical as to our ability to achieve zero discharge for phosphorus pentasulfide but have no data to refute this recommendation.

- 4. Pretreatment guidelines require BPT for dissolved solids. With a zero discharge BPT guideline, this will prohibit joint treatment.
 - 5. Economic data appears grossly understated. Monsanto alone would expect to spend almost \$10 million at nine plants to achieve these levels (if technology were in hand). EPA estimates \$9.3 million for the entire industry.

SPECIFIC PROCESS DETAILS

PHOSPHORUS

Senator Muskie, in Senate consideration of the conference draft of P.L. 92-500, described BPT in the following statements: "The Administrator should establish the range of 'best practicable' levels based upon the average of best existing performance by plants of various sizes, ages, and unit processes within each industrial category." - and - "Best practicable can be interpreted as the equivalent of secondary treatment for industry..." - and - "The balancing test between total cost and effluent reduction benefits is intended to limit the application of technology where the additional degree of effluent reduction is wholly out of proportion to the costs of achieving marginal reduction..."

In this context, we feel that a range of BPT performance should be allowed to include other plants (such as 028 and 159) described as exemplary by the contractor in the light of their 97 - 99%+ removal efficiencies (page 126). Neither has a detectible impact on receiving water quality to offset the very substantial cost (\$3 - 4 million) of achieving zero process discharge.

Accordingly, a guideline range of 0.2 - 0.4 #/ton PO₄, 0.2 - 0.4 #/ton F, 0.5 - 1.0 #/ton TSS and zero elemental phosphorus is recommended.

SODIUM TRIPOLYPHOSPHATE

The proposed rules contend (FR page 24473) that "Zero discharge of process waste water pollutants to navigable waters is being achieved by all of the sodium tripolyphosphate segment." Accordingly no investment or annual costs for compliance are reflected in the economic study.

Monsanto makes almost half of the U.S. production of this product, and we have not achieved zero discharge at any of our five locations. We are trying to demonstrate this capability at one non-food-grade, single-product location. We do not have this technology in hand for either food-grade or multi-product (i.e. calcium, sodium, potassium, and ammonium phosphate) plants.

We have, however, demonstrated advanced phosphate removal treatment (double lime precipitation plus vacuum filtration) at one plant which is identified as exemplary by the contractor (Plant 006 - page 134).

A guideline range of 0.1 - 0.3 $\#/\text{ton PO}_4$ and TSS would reflect this recently installed 95% removal process.

FOOD-GRADE CALCIUM PHOSPHATES

The contractor states that no one has accomplished zero process discharge for this product and, on page 134, indicates how it might be achieved by using several transfers of technology from other products (dry dust collection, polymeric flocculation, lime treatment, and vacuum filtration). We cannot refute these assumptions but can state that the combination is undemonstrated for this process, and is unlikely to be acceptable for food-grade purity. A guideline range similar to sodium tripolyphosphate is recommended.

Mr. John Quarles
Deputy Administrator
U. S. Environmental Protection Agency
Room 1200 West Tower, Waterside Mall
401 M Street, S. W.
Washington, D. C. 20400

Dear Mr. Quarles:

After unsuccessful attempts to make an appointment with you, I am resorting to this less satisfac ory means of personally communicating our deep concern re: proposed zero process discharge guidelines for phosphate chemicals manufacturing.

Personnel in the Office of the Administrator have assured our Environmental Protection staff that you are cognizant of our position and that we've done all we can do. The financial impact of zero discharge by 1977 is so great, however, that we are compelled to exhaust every neans to insure that this problem is recognized at the highest level of EPA. We will, of course, submit detailed comments as prescribed in the Federal Register. The ineffectiveness of our voluminous input to the Effluent Guidelines Division and the Advisory Committee, however, has led us to believe we cannot rely on conventional channels alone.

Our highly condensed position follows.

(1) The contractor's report and virtually identical EPA development document are full of errors and faulty information. No revisions were made as a result of specific and documented critique of these reports. Many plants are claimed to have achieved zero discharge which have not. In several cases the contractor synthesizes 1292 technology by assuming that various techniques from other processes

10/2/73

(1) - Cont'd.

will transfer one to another, and that the undemonstrated combination will work. We believe such an approach should express best available rather than best practicable technology.

- (2) Best practicable standards for phosphorus should consist of a range which includes exemplary plants other than the one which achieves zero. Failure to do so penalizes those who have voluntarily invested in efficient (97-99% plus) end point treatment. Limits of 0.4 lbs per ton phosphate as phosphorus, 0.4 lbs per ton fluoride and 1.0 " per ton suspended solids are recommended.
- (3) Zero process discharge can probably be attained for phosphoric acid, STPP and calcium phosphates provided that treatment and discharge of acid spills and leaks is allowed and the latter two involve non-food grade, single product plants only.
- (4) For treated acid wastes, and food-grade or multi-product phosphates limits of 0.3 lbs per ton for both phosphates and suspended solids are recommended. We do not believe that zero discharge technology is available for these situations.
- (5) The proposed pretreatment standards in 40 CFR 128 when combined with the zero discharge guidelines would prohibit continued or future industrial participation in public treatment.

The economic impact data is grossly understated. Two examples are cited. The actual exemplacy installation upon which most economics are based was our Treaton, Michigan phosphate removal plant. We gave the contractor actual cost details to ding \$700,000 1968 dollars exclusive of sewer separation. The development document estimates investment costs to be less than \$50,000.

Elsewhere, the report states that no investment will be required for STPP in that all 15 plants have already achieved zero. We have established that no more than two or three have done so.

. 3

We feel sure you can appreciate the magnitude of our concern in the light of the above comments. The Federal Register discussion estimated a total compliance cost of 9.2 million dollars for the 80 plants involved. We estimate that we would spend that much on our nine plants alone if we had the technology in hand.

We urgently request that the above comments be reflected in final promulgation of the subject guidelines and/or that the ESWQIAC recommendations be adopted. Cuidelines which represent the range of existing exemplary performance will provide a fair, enforceable basis for timely environmental improvement. Unjustified, unreasonable zero discharge standards will result in unfair economic impact and other exercises which will serve neither government, industry, nor the environment.

Feel free to call me at 314-694-2008 if I may be of service in this matter.

C. P. Cunningham
Vice President & Managing Director
Monsanto Industrial Chemicals Co.

MONSANTO INDUSTRIAL CHEMICALS COMPANY

ST. LOUIS, MISSOURI

COMMENTS ON PROPOSED PHOSPHATE MANUFACTURING EFFLUENT STANDARDS (40 CFR 422-SEPT. 7, 1973 FEDERAL REGISTER) AND

RELATED DEVELOPMENT DOCUMENT (EPA 440/1-73/006)

The Study, upon which the recommended guidelines are based, contains both substantive and incidental inaccuracies. Examples include, but are not limited to, the following:

Federal Register - Page 24473 Par. (vi)(3). "No discharge of process waste water pollutants to navigable waters is being achieved by all of the sodium tripolyphosphate segment. No additional cost is required to maintain this status". The M.CA Task Group, representing the 6 largest producers, has reviewed these comments and identified only two such plants out of the 15 (A. D. Little Study) to 17 (General Technologies Corp. Study) U.S. plants.

Development Document, Sect. I, Page 1, Par. 3 states that "two (plants) have achieved zero discharge of other (than phossy water) process waste waters..." In Chapter IX, Page 127 one of these plants is identified as TVA's who state that they do discharge such wastes and were not contacted by G. T. C.

Sect. I, Page 2, Par. 2 states that "several plants (in the phosphate segment) have already achieved zero discharge...." and on Page 66 (Sect. V)
"Exemplary plant 006 has no process wastes". This plant is Monsanto's Trenton, Michigan phosphate facility. G. T. C. was invited to (and subsequently visited) this plant so that we could make the point that advanced phosphate removal technology - as is employed at Trenton - must be allowed at multi-product, food-grade operations which are not compatible with total recycle. The contractor saw and sampled the discharge from the treatment plant and yet identified it as zero discharge in the report. We question, therefore, the validity of other zero discharge claims in the report.

Sect. XI, Page 147 recommends dissolved solids pretreatment to best practicable levels (i.e. zero), yet also suggests limits of 30 ppm PO₄ and 250 ppm T.S.S. This inconsistency suggests that little thought has been devoted to the impact of "zero" as a pretreatment requirement.

Sect. IX, Page 126 states "Two other phosphorus plants which utilize lime treatment and sedimentation for process water treatment are plants 028 and 159...neither of which recycle treated waste water". Quite to the contrary, these plants (Monsanto's Columbia, Tennessee and Soda Springs, Idaho facilities) totally recycle the streams referred to. G. T. C. inspected both plants at our invitation!

1295

Sect. IX, Page 134 states "The demonstrated practice at Plant 006 (again our Trenton, Michigan Plant), after line treatment for neutralization and precipitation of phosphate wastes, is the direct vacuum filtration of resulting slurry; a practice adopted after gravity settling was judged impractical by plant personne). Vacuum filtration of a reduce the suspended solids content of wastewater from phosphates to the level of 0.5 mg/£...and 0.3 mg/£ dissolved phosphates". During the G. T. C. visit, however, we reported that our experience indicated performance of 50-150 ppm T. S. S. and 3-30 ppm dissolved phosphates. Reporting such performance as "demonstrated" despite written notification 1 of the error well in advance of publication greatly impairs the credibility of the study as a basis for standards development.

The referenced letter also identified 28 other recommended changes or corrections to the contractors report which were not reflected in the development document.

Promulgation of zero process discharge as "best practicable control technology currently available" (BPT) is not justified by the Development Document.

First, we note that in Section 101 of Public Law 92-500, zero discharge of pollutants is a goal for 1985. Also, in Sect. 304 (b)(1)(B), the guidelines for B. P. T. (to be achieved by 1977) are to consider:

- a) The cost in relation to reduction benefits achieved.
- b) Age of equipment and facilities involved.
- c) Process employed.
- d) The engineering aspects of the application of control techniques
- e) Impact on air pollution, solid waste disposal and energy requirements.

Further, the Congressional intent re: the nature of B. P. T. guidelines was expressed by Senator Muskie to wit - "The Administrator should establish the range of 'best practicable' levels based upon the average of the best existing performance by plants of various sizes, ages, and unit processes within each industrial category".

^{1 (}See letter - M. L. Mullins to Dr. Robert G. Shaver (G. T. C.) and Mr. Elwood Martin (EPA Project Officer) dated July 18, 1973).

Page 169, Volume 1, "A Legislative History of the WPCA Amendment of 1972.

We contend that the zero process discharge effluent standards proposed go far beyond the intent of what was intended by 1977; do not, in fact, consider the factors required by the law; and do not, in any way, represent the range of best existing performance. Further, zero discharge dictates total recycle as treatment technology rather than allow a choice of adequate alternative technologies as EPA has often stated as a commendable objective.

Plants 006, 028 and 159 are described by the contractor as "exemplary," 3 as "achieving very high (97-99%) removal of pollutants" 4 and as "achieving very low levels to TSS and TDS". 5

Zero process discharge standards which would prohibit continued use of such treatment investments will penalize those who have, in many cases voluntarily and quite recently, acted in good faith.

No discussion is found in the Background Document which evaluates the high cost of going from 97-99% + removal to zero discharge as compared to the minimal benefits achieved.

No determination is found of the age of the few (4?) existing zero discharge plants. It's realistic to build a new zero discharge plant for some of the products covered, but in many cases it is physically impossible to convert older plants with integrated sewer systems and end point treatment to total recycle.

Process differences such as solution vs. slurry fed STPP, food-grade vs. f. technical grade STPP and calcium phosphates, arid vs. high rainfall geography, and single product vs. multi-product configuration, are not reflected, except that to point out that the single zero discharge phosphorus vio plant does discharge when it rains!

Impact on non-water environmental concerns is mentioned but not really considered in the determination of B. P. T. For example one of our plants proposes to convert from wet to dry dust collection which will reduce raw waste loading. The contractor was shown the pilot installation - and particularly the natural gas heater required to raise the temperature of the moisture saturated dust laden gas stream sufficiently to prevent blinding of bags. This natural gas requirement - which has subsequently raised serious questions re: project viability - was not mentioned, although conversion to bag collectors was recommended as B. P. T. Likewise, our experience with P2O5 and phosphine furning from ponds where phossy water is treated with lime was not mentioned.

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Sect. V, Page 66

Sect. IX, Page 126

Sect. IX, Page 134

Our experience with placehote removal via lime precipitation/vacuum filtration (Plant 606) vaccom we were "kicked out" of sanitary landfills because the resulting wind waste is over the frequently adopted 50% moisture limit was not related.

Finally, it is obvious the various process discharge does not represent the "range of existing B. M. L. for the various sizes, ages and processes".

Not one plant has achieved hero in the phosphorus derivatives group (P2O5, P2S5, PCl3, POCl3). There process discharge technology for calcium phosphates is a chieved by "synthesized" by assuming that five distinct process changes, undemonstrated for this process, will work (dry dust collection of dayer off-gas, lime precipitation of calcium phosphates, vacuum filtration, polymeric flocculation and recycle of resulting effluents back to a food-grade process). Monsanto has tried parts of this assemblage and encountered formidable difficulties not yet overcome.

Monsanto has provided substantial input to, and participated in four hearings of the Effluent Standards and Water Quality Information Advisory Committee (ESWQIAC). This committee has consistently pushed industry to put its best technical foot forward, and have also exhibited a high degree of scientific competence in both treatment technology and water quality criteria. Concurrently, however, they have agreed that the program of work between now and 1977 should not be to penalize those who have already, in good faith, installed adequate treatment, but to provide requirements to insure that those with little or no abatement correct gross, untreated discharges on a timely basis.

This committee submitted comments on the contractors draft dated August 31 which stated that "the guideline of zero discharge...for the three segments is not BPT and it should not be the Level I guideline". Further, numerical values are proposed for the significant wastes from the industry (P, PO₄, F, and T.S.S.) which, while requiring some expenditures for the exemplary plants which utilize end point treatment rather than total recycle, are deemed reasonable by our Company as well as those represented by the MCA Task Group. Monsanto strongly urges adoption of these values as Level I technology:

| PO4 (as P) | 0.2 - 0.4 lb/ton |
|-------------|------------------|
| F | 0.2 - 0.3 lb/ton |
| T. S. S. | 0.5 - 1.0 lb/ton |
| Elemental P | Zero |

Table 18, Page 109, Sect. VIII.

⁷ Sect. IX, Page 134.

⁸ ESWQIAC Final Report to Administrator, U.S. EPA re: Proposed Phosphate Manufacturing Effluent Standards, 8/31/73.

 Zero discharge standards are incompatible with proposed 40 CFR 128 pretreatment standards.

Aside from the inconsistencies pointed out earlier re; establishing a zero discharge pretreatment limit on dissolved solids and allowing 30 and 250 ppm respectively of PO₄ and T.S.S., Monsanto contends that any pretreatment requirement for PO₄, suspended solids and dissolved solids is inappropriate. The EPA guidelines entitled "Pretreatment of Discharges to Publicly Owned Treatment Works" (1973 546-308/30 1-3) states in Table D-21-2, Page D-17-11, that no pretreatment is recommended for STPP! This total inconsistency (total recycle vs. no treatment) is very disconcerting. Four of our five phosphoric acid/phosphate salts plants presently participate in municipal systems. Suspended solids are, of course, removed in municipal biological treatment.

Dissolved solids are of no environmental significance nor is practicable treatment technology available. Phosphate removal, per EPA policy, is best practiced at the municipal level and only in those cases where entrophication problems justify such removal.

In short, no argument is made for <u>any</u> pretreatment, much less total recycle! Pretreatment standards which would prohibit continued or future industrial participation in joint treatment would clearly be contrary to the intent of Congress.

V. Economic data which is offered to support zero discharge is understated by as much as a factor of twenty.

The validity of Supplement A of the G. T. C. report (Cost Data) is in our opinion, so questionable as to void the conclusions of the A. D. Little Economic Impact Study.

For example, no investment or operating cost is reflected for the entire STPP segment! As stated earlier, none of Monsanto's five facilities have achieved zero process discharge (although two discharge only to municipal systems, i.e. - not to navigable waters). The MCA Task Group estimates that only two of the 15-17 U.S. plants have eliminated process discharges. To assume, in such a highly competitive commodity, that the investment required to convert to total recycle would be cost savings justified is unrealistic. For example, our Trenton, Michigan complex loses less than \$100 worth of product per day which would justify no more than a \$75,000 investment (based on 10 year depreciation, 20% O&M and 10% minimum after tax return on investment) if 100% of the loss were recoverable! While we don't know how to achieve total recycle for this multi-product, food-grade plant, we conservatively estimate the cost of the contractor's rationale at ten times that justified above.

For most all of the products covered, sewer separation (i.e.: non-contact vs. process), lime treatment, clariflocculation, vacuum filtration of underflow, Landfill of sludge, settling pends with polymeric addition to clarify overflow and recycling facilities (i.e.: pumps and lines) are stipulated. Supplement "A" estimates the cost of such facilities at \$0 (STPP) to \$50,000 (P₂S₅) for the representative plants. Monsanto gave the contractor actual cost data for all but the polymer addition, recycle facilities and sewer separation work, and the total was 700,000 1968 dollars. Today's cost for the total system would probably be from 1.5 to \$2.0 M! Why this actual cost data, which was furnished the contractor and is included in the public record in Supplement B, was not reflected is inexplicable.

A final example. The cost of converting phosphorus Plant 028 to total recycle is estimated at \$500,000 based on pumping the plant's effluent 1,000 yds. to the plant's intake! Such a simplistic approach borders on the ridiculous. Our estimate for converting the three process systems employing end point treatment (slag quenching, raw material dust collection and coke handling dust collection) to total recycle is \$2.4M 9, although the technology assumed in the estimate is undemonstrated. This expenditure would improve the following treatment efficiencies to 100%:

| TSS | 99. 97% | |
|-----------------|---------|-----------------------|
| TDS | 99. 98% | See Note 9 for Source |
| F | 99. 98% | |
| PO ₄ | 99.6% | |
| P (elemental) | 100 % | |

Analysis of river water above and below this plant show no detectable increase of these parameters 10-i.e. - no water quality improvement will occur to justify the abatement expenditure.

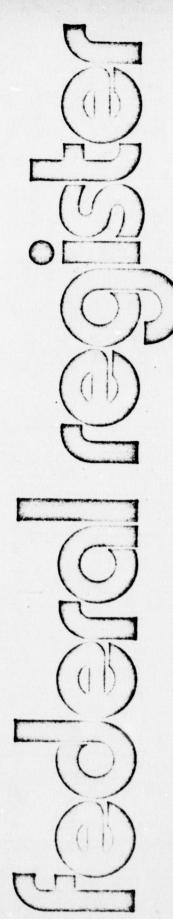
It should be pointed out that this plant is recognized as exemplary and its cost of meeting total process recycle would probably be considerably less than typical for the other eight U.S. plants.

⁹ Monsanto data transmittal to ESWQIAC dated July 28, 1973.

Monsanto data transmittal to ESWQIAC dated April 30, 1973.

All of this data was furnished EPA, ESWQIAC or the contractor - see reference footnotes.

The Economic Impact Report states "If actual costs to achieve zero discharge are significantly higher than indicated in the effluent guideline document, as a number of producers believe to be the case, significant economic impacts may be felt". We certainly concur, suggesting that the input data is low by factors of 5 to 20 and more in the case of the no-cost estimate for STPP.



WEDNESDAY, FEBRUARY 20, 1974 WASHINGTON, D.C.

Volume 39 Number 35

PART II



ENVIRONMENTAL PROTECTION AGENCY

PHOSPHATE
MANUFACTURING POINT
SOURCE CATEGORY

Effluent Guidelines and Standards

Title 40—Protection of the Environment
CHAPTER I—ENVIRONMENTAL
PROTECTION AGENCY

SUBCHAPTER N-EFFLUENT GUIDELINES AND STANDARDS

PART 422—PHOSPHATE MANUFACTUR-ING POINT SOURCE CATEGORY

Effluent Limitation Guidelines

On September 7, 1973 notice was published in the FEDERAL REGISTER (38 FR 24470), that the Environmental Protection Agency (EPA or Agency) was proposing effluent limitations guidelines for existing sources and standards of performance and pretreatment standards for new sources within the phosphorus producing, phosphorous consuming and phosphate subcategories of the phosphate manufacturing category of point sources. The purpose of this notice is to effluent limitations establish final guidelines for existing sources and standards of performance and pretreatment standards for new sources in the phosphate manufacturing category of point sources, by amending 40 CFR Chapter I, Subchapter N, to add a new Part 422. This final rulemaking is promulgated pursuant to sections 301, 304 (b) and (c), 306 (b) and (c) and 307(c) of the Federal Water-Pollution Control Act, as amended, (the Act); 33 U.S.C. 1251, 1311, 1314 (b) and (c), 1316 (b) and (c) and 1317(c) 86 Stat. 816 et seq.; Pub. L. 92-500. Regulations regrading cooling water intake structures for all categories of point sources under section 316(b) of the Act will be promulgated in 40 CFR Part 402.

In addition, the EPA is simultaneously proposing a separate provision which appears in the proposed rules section of the FEDERAL REGISTER, stating the application of the limitations and standards set forth below to users of publicly owned treatment works which are subject to pretreatment standards under section 307(b) of the Act. The basis of that proposed regulation is set forth in the associated notice of proposed rulemaking.

The legal basis, methodology and factual conclusions which support promulgation of this regulation were set forth in substantial detail in the notice of public review procedures published August 6. 1973 (38 FR 21202) and in the notice of proposed rulemaking for the phosphate manufacturing category. In addition, the regulations as proposed were supported by two other documents: (1) The document entitled "Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the PHOSPHOROUS DERIVED CHEMICALS Segment of the Phosphate Manufacturing Point Source Category" (August 1973) and (2) the document entitled "Economic Analysis of Proposed Effluent Guidelines, The In-dustrial Phosphate Industry" (August 1973). Both of these documents were made available to the public and circulated to interested persons at approximately the time of publication of the notice of proposed rulemaking.

Interested persons were invited to

participate in the rulemaking by submitting written comments within 30 days from the date of publication. Prior public participation in the form of solicited comments and responses from the States, Federal agencies, and other interested parties were described in the preamble to the proposed regulation. The EPA has considered carefully all of the comments received and a discussion of these comments with the Agency's response thereto follows.

The regulation as promulgated contains some significant departures from the proposed regulation. The following discussion outlines the reasons why these changes were made and why other suggested changes were not made.

(a) Summary of comments.

The following responded to the request for written comments contained in the preamble to the proposed regulation: Mobil Oil Corporation: FMC Corporation: Manufacturing Chemists Association: Stauffer Chemical Company; Hooker Industrial Chemicals: University of Florida, Institute of Food and Agricultural Sciences; Pasaic Valley Sewerage Commissioners; County Sanitation District of Los Angeles County; U.S. Department of Commerce; and Monsanto Industrial Chemicals Company. Each of the comments received was carefully reviewed and analyzed. The following is a summary of the significant comments and the Agency's response to those comments.

(1) It was stated by several commenters that a no discharge guideline legally could not be applied until 1985.

EPA has determined that in the case of certain subcategories of the phosphate manufacturing category, either the best practicable control technology currently available or the best available technology economically achievable is the total recirculation of process waste water. In section 101(a)(2) of the Act. Congress established as a national goal the elimination of the discharge of pollutants into navigable waters by 1985. However, Congress also set requirements for technology based standards in sections 301, 304(b) and 306 which require the maximum degree of reduction of pollutant discharges prior to 1985, which is consistent with the technical and economic factors to be taken into account under sections 304(b) and 306 of the Act (notably, standards are to be set for 1977 and 1983 compliance, but no regulations are to be promulgated for 1985). The Agency will require the effluent reduction attainable by the best practicable control technology when establishing regulations under section 304(b) of the Act whether that reduction is to some degree of permitted discharge or down to no discharge.

(2) It was commented that best practicable control technology currently available should be based on a large number of plants if not the entire industry.

The Agency defines best practicable control technology currently available to be the average of the best existing performance by plants of various sizes, ages and unit processes within each industrial

category or subcategory. This average is not based upon a broad range of plants within an industrial category or subcategory, but is based upon performance levels achieved by exemplary plants. In those industrial categories where present control and treatment practices are uniformly inadequate, a higher level of control than any currently in place may be required if the technology to achieve such higher level can be practicably applied by July 1, 1977. Thus best practicable control technology currently available may be based on a few, one or no exemplary plants within that industrial category.

(3) Several commenters pointed out that runoff cannot be kept out of treatment ponds in some terrain and that a state of no discharge cannot be met dur-

ing periods of heavy rainfall.

Treatment ponds can be built or modified to minimize, if not eliminate, intrusion of storm runoff originating outside of the pond retaining walls. Such ponds can also have sufficient free board as to retain rainfall. Those subcategories which employ treatment ponds are water consuming processes which can utilize the captured rainfall. Hence, there should be no need to discharge pond water.

(4) It was mentioned that the recycle of process waste water for food grade calcium phosphates would cause the Food and Drug Administration (FDA) specifications for process water to be violated.

Water is used in the manufacture of food grade calcium phosphates for reasons of transport or homogeneity, but not for purification. Hence the waster contains the product, but nothing harmful to the product, which is what the FDA specifications are designed to protect.

The problem of segregation of waste waters, water balances, and storm water runoff, however, are sufficiently great that the industry will not be able to achieve total recycle by 1977 and yet meet FDA specifications. A discharge will therefore be allowed after suitable treatment as demonstrated in the Development Document.

(5) It was suggested that a limitation for dissolved solids be dropped for best practicable control technology currenily available, since in the concentration range of the constituents involved, technology to achieve the proposed degree of

control does not exist.

The limitation proposed was based on the raw waste load and was not intended to force treatment of dissolved solids. The limitation was intended to prehibit additional dissolved solids from being discharged. However, due to variability in the process this limitation may require such treatment. Therefore, the limitation on dissolved solids is replaced by limits on specific dissolved constituents that are considered to be the principal pollutants or characteristics to be controlled.

(6) It was suggested that the limits preposed by the Effuent Standards and Water Quality Information Advisory Committee (ESWQIAC) for the phos-

phorus production subcategory be used.

The ESWQIAC limits include two additional phosphorus plants as exemplary. EPA has since accepted these plants as exhibiting best practicable control technology and has allowed a discharge based upon the data in the Development Document for the treatment capabilities of these plants. Therefore, although the Agency does not agree with the underlying rationale for establishing the ESWQIAC limits, the data in the Development Document does support the specific limits proposed by ESWQIAC.

(7) It was requested that discharges to publicly owned treatment works be

Pretreatment and discharge of waste waters to publicly owned treatment works from existing sources in the phosphate category are covered in the pretreatment guidelines that are proposed at the time this limitation is promulgated. Comments relating to existing sources should be directed to that regulation. For new sources the Agency considers the process waste water constituents from the phosphorus production and phosphorus consuming subcategories to be incompatible with publicly owned treatment works, and that the treatment technology that has been described in Section VII of the Development Document can achieve no discharge of process waste water pollutants to either navigable waters or to publicly owned treatment works.

The principal process waste water pollutant for the phosphate subcategory is phosphate, which cannot be adequately treated by primary or secondary treatment works. Phosphate, however, is considered to be compatible with publicly owned treatment works designed, constructed and operated to achieve optimal removal of dissolved phosphate, and a discharge to such treatment works will

be allowed.

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(8) Several commenters considered the capital costs of the model treatment systems to be underestimated and that the economic impact is understated.

The Agency has recalculated, in Section VIII of the Development Document, the cost information on model treatment systems as the result of additional data submitted by industry. The calculated changes do not affect the conclusions of the economic analysis, since the percentage increase in capital cost is not significant.

(9) It was stated that some plants were incorrectly cited as to whether they were

achieving no discharge or not.

The necessary qualifiers were added to the descriptions in the Development Document of those plants that were disputed. The changes that were made involved treatment of certain portions of the process waste water and do not substantially affect the overall conclusions of the Development Document.

(10) The general comment was made that zero discharge cannot be achieved for some products.

The Agency has reevaluated the data

and is allowing a discharge for phosphorus and food grade calcium phosphates production for the 1977 limitation for the reasons given in comments (4) and (6). The Agency believes the technology exists to substantiate a no discharge of process waste water limitations for the remaining manufacturing processes.

(11) A range of values was recommended rather than a single value for

each parameter.

The Agency considers that the limitations already represent ranges, taking into account differences in process, age. size and other factors. Subcategorization has been done to take these factors into account with different limitations for each subcategory. Within subcategories, exceptions to the limitations have been made for certain manufacturing segments or products, constituting a wider range. Each numerical limitation represents a maximum average of daily values over a given period of time. This in effect represents a range from zero up to the specific limitation. A maximum varia-tion is also given for each maximum average limitation. The Agency considers an upper and lower limitation to be somewhat meaningless since the actual range would be from zero to the upper limitation. Thus, in effect, the argument becomes one of making the EPA limitations less severe, since it has been suggested that the EPA limitations should be the lower limits. The EPA limitations are achievable and currently available.

(12) One commenter stated that there is no correlation of contractor validation data with data or conclusions contained

in the Development Document.

Data calculated from samples collected by the contractor were not primarily intended to form the basis of a limitation. The validation data was mainly used by the contractor to determine if existing data can be correctly used to establish limitations. Such a correlation does not appear in the Development Document, but the raw data may be reviewed at the EPA Information Center. Room 227, West Tower. Waterside Mall, Washington, D.C. Only the data that appears in the Development Document was used in formulating the effluent limitations.

(13) It was stated that the evaporation of PCl3 and POCl3 process waste waters would require an excessive

amount of energy.

The 1983 limitations for the manufacture of PCl3 and POCl3 are no discharge of process waste water pollutants which can be accomplished by maximum waste water recycle and evaporation of the blowdown. The Agency believes that sufficient time exists for each plant to be examined by the industry in order to minimize water usage, maximize solar evaporation and thus minimize power usage.

(14) It was pointed out that percolation can occur from waste water ponds.

Infiltration of pond water to ground water cannot be controlled by this regulation. Possible problems have been pointed out in the preamble to the proposed regulation (38 FR 24470) and

methods of correction have been suggested.

(15) The comment was made that no discharge of process waste water pollutants is an impractical limitation because the methods of analysis are not sufficiently sensitive.

Where no discharge of process waste water pollutants is prescribed, model treatment systems are described in the Development Document in which no process waste waters are discharged, hence no process waste waters pollutants. For the purpose of determining if process waste water pollutants have contaminated other allowable discharges, this limitation is considered to be the detectable limit of the appropriate analytical method.

(16) It was suggested that no discharge of process waste water pollutants should mean no discharge that would degrade the quality of the receiving stream.

The Act is quite specific in stating the difference between limitations based on treatment technology and limitations handled on a case by case basis in order to insure that water quality standards are attained. The limitations promulgated in this regulation are technology based and independent of water quality standards, as is the intent of the Act.

(17) It was suggested that concentrations (mg/1) should be used with instantaneous maximum values instead of

production based limitations.

Production based limitations such as kg of pollutant per kkg of product insure that dilution is not practiced. Daily maximum values are also promulgated.

(18) One commenter stated that phosphate limitations for the phosphate industry are unduly restrictive when compared to phosphate limitations for publicly owned treatment works.

The Act establishes separate time tables for industrial and municipal sources. Limitations for phosphate discharges from publicly owned treatment works will be proposed at a later date. However, effluent guidelines for industrial sources are to be based on the best practicable, best available, and best demonstrated technologies for each separate category and separate economic considerations for each category.

(19) One company agreed with the proposed limitation for the manufacture of phosphoric acid, phosphorous trichloride and phosphorous oxychloride.

(20) Another company suggested that no discharge of process waste water pollutants for the manufacture of phosphorus, sodium tripolyphosphate and food grade calcium phosphate is the best available technology rather than the best practicable control technology.

The Agency has reviewed the data and agrees that a discharge resulting from the manufacture of phosphorus and food grade calcium phosphate should be allowed for the 1977 limitations for the reasons listed in comments (4) and (6). However no discharge of process waste water pollutants still qualifies as best practicable control technology currently

available for the manufacture of sedium tripolyphosphate.

(b) Revision of the proposed regulation prior to promulgation.

As a result of public comments and continuing review and evaluation of the proposed regulation by the EPA, the following changes have been made in the regulation.

(1) Minor adjustments have been made to reflect the fact that an increased number of definitions and analytical methods have been included in 40 CFR 401 and are incorporated by reference in 40 CFR 401 and are incorporated by reference in these subparts.

(2) A discharge will be allowed for the 1977 limitation for the phosphorus production subcategory. This change was made in response to comments (2), (6), (10) and (20) in section (a) above. The limitation, are based upon two plants that discharge process waste water from treatment facilities exhibiting exemplary performance.

(3) The total dissolved solids limitations for the manufacture of phosphorus trichloride and phosphorus oxychloride have been replaced with limitations on specific dissolved species. This change was made in response to comment (5) in section (a) above.

(4) A discharge will be allowed for the 1977 limitation for the manufacture of food grade calcium phosphate. The reasons for this change are listed in comments (4), (6) and (20). The limitations are based upon the volume of water used in the process and the technological capability of treating suspended solids and total phosphorus.

(5) Section 304(b)(1)(B) of the Act provides for "guidelines" to implement the uniform national standards of Section 301(b)(1)(A). Thus Congress recognized that some flexibility was necessary in order to take into account the complexity of the industrial world with respect to the practicability of pollution control technology. In conformity with the Congressional intent and in recognition of the possible failure of these regulations to account for all factors bearing on the practicability of control technology, it was concluded that some provision was needed to authorize flexibility in the strict application of the limitations contained in the regulation where required by special circumstances applicable to individual dischargers. Accordingly, a provision allowing flexibility in the application of the limitations representing best practicable control technology currently available has been added to each subpart, to account for special circumstances that may not have been adequately accounted for when these regulations were developed.

(c) Economic impact.

The changes that were made to the proposed regulations for the phosphate category do not substantially affect the initial economic analysis. These changes center about the feasibility of recycling treated process waste water rather than different treatment systems. Additional cost data was received from the phos-

phate manufacturing industry, and a careful review of the costs of alternate treatment technologies was performed. Appropriate upward changes to the cost estimates were made in Section VIII of the Development Document. These changes likewise do not affect the conclusions of the economic impact study, since the cost increases are minimal.

(d) Cost-benefit analysis.

The detrimental effects of the constituents of vaste waters now discharged by point sources within the phosphorus production subcategory, phosphorus consuming subcategory and the phosphate subcategory of the phosphate manufacturing point source category are discussed in Section VI of the report entitled "Development Document for Effluent Limitations Guidelines for the PHOSPHORUS DERIVED CHEMICALS Manufacturing Segment of the Phosphate Manufacturing Point Source Category" (February 1974). It is not feasible to quantify in economic terms, particularly on a national basis, the costs resulting from the discharge of these pollutants to our Nation's waterways. Nevertheless, as indicated in Section VI, the pollutants discharged have substantial and damaging impacts on the quality of water and therefore on its capacity to support healthy populations of wildlife, fish and other aquatic wildlife and on its suitability for industrial, recreational and drinking water supply uses.

The total cost of implementing the effluent limitations guidelines includes the direct capital and operating costs of the pollution control technology employed to achieve compliance and the indirect economic and environmental costs identified in Section VIII and in the supplementary report entitled "Economic Analysis of Proposed Effluent Guidelines for the INDUSTRIAL PHOSPHATE IN-DUSTRY" (August 1973). Implementing the effluent limitations guidelines will substantially reduce the environmental harm which would otherwise be attributable to the continued discharge of polluted waste waters from existing and newly constructed plants in the phosphate manufacturing industry. Agency believes that the benefits of thus reducing the pollutants discharged justify the associated costs which, though substantial in absolute terms, represent a relatively small percentage of the total capital investment in the industry.

(e) Publication of information on processes, procedures or operating methods which result in the elimination or reduction of the discharge of pollutants.

In conformance with the requirements of section 304(c), a manual entitled, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the PHOS-PHORUS DERIVED CHEMICALS Segment of the Phosphate Manufacturing Point Source Category," has been published and is available for purchase from the Government Printing Office, Washington, D.C. 20401, for a nominal fee.

(f) Final rulemaking.

In consideration of the foregoing, 40

CFR Chapter I, Subchapter N is hereby amended by adding a new Part 422, Phos-

phate Manufacturing Point Source Category, to read as set forth below. This final regulation is promulgated as set forth below and shall be effective April 22, 1974.

Dated: January 31, 1974.

JOHN QUARLES.
Acting Administrator.

Subpart A-Phosphorus Production Subcategory

Sec.

422.10 Applicability; description of the phosphorus production subcategory.

422.11 Specialized definitions.

422.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the applicacation of the best practicable control technology currently available.

422.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

422.14 Reserved.

422.15 Standards of performance for new sources.

422.16 Pretreatment standards for new sources.

Subpart B-Phosphorus Consuming Subcategory

422.20 Applicability; description of the phosphorus consuming subcategory.

422.21 Specialized definitions.

22.22 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

422.23 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

422.24 Reserved.

422.25 Standards of performance for new sources.

422.26 Pretreatment standards for new sources.

Subpart C-Phosphate Subcategory

422.30 Applicability; description of the phosphate subcategory.

422.31 Specialized definitions.

422.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

422.33 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

422.34 Reserved.

422.35 Standards of performance for new sources.

422.36 Pretreatment standards for new sources.

Subpart A—Phosphorus Production Subcategory

§ 422.10 Applicability; description of the phosphorus production subcategory.

The provisions of this subpart are applicable to discharges of pollutants re-

eli:

pH.

sulting from the production of phosphorus and ferrophosphorus by smelting of phosphate ore.

§ 122.11 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR 401 shall apply to this subpart.

§ 422.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

In establishing the limitations set forth in this section. EPA took into account all information it was able to collect, develop and solicit with respect to factors (such as age and size of plant, raw materials, manufacturing processes, products produced, treatment technology available. energy requirements and costs) which can affect the industry subcategorization and effluent levels established. It is, however, possible that data which would af-fect these limitations have not been available and, as a result, these limita-tions should be adjusted for certain plants in this industry. An individual discharger or other interested person may submit evidence to the Regional Administrator (or to the State, if the State has the authority to issue NPDES permits) that factors relating to the equipment or facilities involved, the process applied, or other such factors related to such discharger are fundamentally different from the factors considered in the establishment of the guidelines. On the basis of such evidence or other available information, the Regional Administrator (or the State) will make a written finding that such factors are or are not fundamentally different for that facility compared to those specified in the Development Document. If such fundamentally different factors are found to exist, the Regional Administrator or the State shall establish for the discharger effluent limitations in the NPDES permit either more or less stringent than the limitations established herein, to the extent dictated by such fundamentally different factors. Such limitations must be apoved by the Administrator of the Environmental Protection Agency. The Administrator may approve or disapprove such limitations, specify other limitations, or initiate proceedings to revise these regulations.

The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available:

| | Effluent limitations | |
|--------------------------|--------------------------|-----------------------------------------------------------------------------|
| Effluent tracteristic | Maximum for any I day | Average of daily values for 30 consecutive days shall not exceed - |

Metric units (kg kkg of product)

| | *** | | |
|----------------------------|-------------------------|---------------------|--|
| T88. | 1.0 | 0.5 | |
| Total phosphorus | . 30 | . 15 | |
| Fluoride | . 10 | , as | |
| Elemental phos- phorus. | No detectable quantity. | | |
| pft | Within the ram | 6.0 to 9.0. | |
| | English units (Ib/1 | ,000 (b of product) | |
| T88 | 1.0 | 0.5 | |
| Total phosphorus . | . 30 | . 15 | |
| Finoride | . 10 | .05 | |
| Elemental phos- | No detectable quantity. | | |

§ 422.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

.... Within the range 6.0 to 9.0,

The following limitations establish the quantity or quality of pollutants or pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.14 [Reserved]

§ 422.15 Standards of performance for new sources.

The following standards of performance establish the quantity or quality of pollutants or pollutant properties which may be discharged by a new source subject to the provisions of this subpart: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.16 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act for a source within the phosphorus production subcategory, which is a user of a publicly owned treatment works (and which would be a new source subject to section 206 of the Act, if it were to discharge pollutants to the navigable waters), shall be the standard set forth in 40 CFR Part 128, except that, for the purpose of this section, § 128.133 of this title shall be amended to read as follows:

"In addition to the prohibitions set forth in 40 CFR 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works shall be the standard of performance for new sources specified in 40 CFR 422.15; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the

pretreatment standard applicable to users of such treatment works shall, except in the case of standards providing for no discharge of pollutants, be correspondingly reduced in stringency for that pollutant."

Subpart B—Phosphorus Consuming Subcategory

§ 122.20 Applicability; description of the phosphorus consuming subcategory.

The provisions of this subpart are applicable to discharges of pollutants resulting from the manufacture of phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride directly from elemental phosphorus. The production of phosphorus trichloride and phosphorus oxychloride creates waste water pollutants not completely amenable to the procedures utilized for best practicable control technology currently available. The standards set for phos-phorus trichloride manufacture and phosphorus oxychloride manufacture, accordingly, must differ from the rest of the subcategory at this level of treatment.

§ 422.21 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR Part 401 shall apply to this subpart.

§ 422.22 Effluent limitations guidelines, representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

In establishing the limitations set forth in this section, EPA took into account all information it was able to collect, develop and solicit with respect to factors (such as age and size of plant, raw materials, manufacturing processes, products produced, treatment technology available. energy requirements and costs) which can affect the industry subcategoriza-tion and effluent levels established. It is, however, possible that data which would affect these limitations have not been available and, as a result, these limitations should be adjusted for certain plants in this industry. An individual discharger or other interested person may submit evidence to the Regional Administrator (or to the State, if the State has the authority to issue NPDES permits) that factors relating to the equipment or facilities involved, the process applied, or other such factors related to such discharger are fundamentally different from the factors con sidered in the establishment of the guidelines. On the basis of such evidence or other available information, the Regional Administrator (or the State) will make a written finding that such factors are or are not fundamentally different for that

Incility compared to those specified in the Development Document. If such fundamentally different factors are found to exist, the Regional Administrator or the State shall establish for the discharger effluent limitations in the NPDES permit either more or less stringent than the limitations established herein, to the extent dictated by such fundamentally different factors. Such limitations must be approved by the Administrator of the Environmental Protection Agency. The Administrator may approve or disapprove such limitations, specify other limitations, or initiate proceedings to revise these regulations.

The following limitations establish the quantity or quality of pollutants or pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available:

(a) There shall be no discharge of process waste water pollutants to navigable waters from the manufacture of phosphoric acid, phosphorus pentoxide, or phosphorus pentasulfide.

(b) The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this paragraph, which may be discharged in process waste water from phosphorus trichloride manufacturing on the basis of production:

| | Effluent limitations | | |
|------------------------------------------------------|-------------------------------------------|-----------------------------------------------------------------------------|--|
| Effluent characteristic | Maximum for any 1 day | Average of daily values for 30 consecutive days shall not exceed - | |
| | Metric units (kg/kkg of product) | | |
| TSS. Total phosphorus Arsenic. Elemental phosphorus. | 1.4 1.6 .0001 No detectable o | | |
| pff | Within the range 6.0 to 9.0. | | |
| • | English units (lb/1,000 lb of product) | | |
| T88 | 1. 4 1. 6 .0001 No detectable of | 0.7 0.8 . 00005 puantity. | |
| phorus. | . Within the range 6.0 to 9.0. | | |

(c) The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this paragraph, which may be discharged in process waste water from phosphorus oxychloride manufacturing on the basis of production:

Effluent amitations

| Effluent characteristic | Maximum for any 1 day | Average of daily values for 30 consecutive days shall not exceed— |
|---------------------------------|----------------------------------|----------------------------------------------------------------------------|
| | Metric units (kg/kkg of product) | |
| T88. Total phosphorus pll | .31 | 0, 15 17 to 6.0 to 9.0. |
| i i | English units (lb. | (1,000 lb of product) |
| T88 | 0.3 .3t Within the rang | 0. 15 17 te 6.0 to 9.0. |

§ 122.23 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

The following limitations establish the quantity or quality of pollutants or pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology economically achievable: there shall be no discharge to navigable waters of process waste water pollutants to resulting from the manufacture of phosphoric acid, phosphorus pentoxide, phosphorus pentoside, phosphorus or phosphorus oxychloride.

§ 422.21 [Reserved]

§ 422.25 Standards of performance for new sources.

The following standards of performance establish the quantity or quality of pollutants or pollutant properties which may be discharged by a new source subject to the provisions of this subpart: There shall be no discharge of process waste water pollutants to navigable waters.

§ 422.26 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act for a source within the phosphorus consuming subcategory, which is a user of a publicly owned treatment works (and which would be a new source subject to section 306 of the Act, if it were to discharge pollutants to the navigable waters), shall be the standard set forth in 40 CFR Part 128, except that, for the purpose of this section, § 128.133 of this title shall be amended to read as follows:

"In addition to the prohibitions set forth in 40 CFR 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works shall be the standard of performance for new sources specified in 40 CFR 422.25; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall, except in the case of standards providing for no discharge of pollutants, be correspondingly reduced in stringency for that pollutant."

Subpart C-Phosphate Subcategory

§ 422.30 Applicability; description of the phosphate subcategory.

The provisions of this subpart are applicable to discharges of pollutants resulting from the manufacture of sodium tripolyphosphate, animal feed grade, calcium phosphate and human food grade calcium phosphate from phosphoric acid. The production of human food grade calcium phosphate creates waste water pollutants not completely amenable to the procedures utilized for best practicable control technology currently available. The standards set for human food grade calcium phosphates accordingly must

differ from the rest of the subcategory at this level of treatment.

§ 122.31 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR 401 shall apply to this subpart.

§ 422.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

In establishing the limitations set forth in this section. EPA took into account all information it was able to collect, develop and solicit with respect to factors (such as age and size of plant, raw materials, manufacturing processes, prodproduced, treatment technology available, energy requirements and costs) which can affect the industry subcategorization and effluent levels established. It is, however, possible that data which would affect these limitations have not been available and, as a result, these limitations should be adjusted for certain plants in this industry. An individual discharge or other interested person may submit evidence to the Regional Administrator (or to the State, if the State has the authority to issue NPDES permits) that factors relating to the equipment or facilities involved, the process applied. or other such factors related to such discharger are fundamentally different from the factors considered in the establishment of the guidelines. On the basis of such evidence or other available information, the Regional Administrator (or the State) will make a written finding that such factors are or are not fundamentally different for that facility compared to those specified in the Development Document. If such fundamentally different factors are found to exist, the Regional Administrator or the State shall establish for the discharger effluent limitations in the NPDES permit either more or less stringent than the limitations established herein, to the extent dictated by such fundamentally different factors. Such limitations must be approved by the Administrator of the Environmental Protection Agency. The Administrator may approve or disapprove such limitations, specify other limitations, or initiate proccedings to revise these regulations.

The following limitations establish the quantity or quality of pollutants or pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best practicable control technology currently available:

(a) There shall be no discharge of process waste water pollutants to navigable waters from the manufacture of sodium tripolyphosphate, or animal feed grade calcium phosphate.

(b) The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this paragraph, which may be discharged in process waste water from human food grade calcium phosphate manufacturing based on production:

| Effluent characteristic | Maximum for any I day | Average of daily values for 30 consecutive days shall not exceed | | |
|-------------------------------|--------------------------------------|---------------------------------------------------------------------------|--|--|
| | Metric units (kg/kkg of product) | | | |
| TSS Total phosphorus pH | 0. 12 .06 Within the rang | 0.05 .03 te 6.0 to 9.0. | | |
| | English units (lb/1,000 lb of produc | | | |
| TSS | 0. 12 .06 Within the rang | 0.06 .03 ge 6.0 to 9.0, | | |

Effluent limitations

§ 422.33 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

The following limitations establish the the quantity or quality of pollutants or pollutant properties which may be discharged by a point source subject to the provisions of this subpart after application of the best available technology

economically achievable: There shall be no discharge to navigable waters of process waste water pollutants resulting from the manufacture of sodium tripolyphosphate, animal feed grade calcium phosphate, or human food grade calcium phosphate.

§ 422.34 [Reserved]

§ 422.35 Standards of performance for new sources.

The following standards of performance establish the quantity or quality of pollutants or pollutant properties which may be discharged by a new source subject to the provisions of this subpart: There shall be no discharge of process waste water pollutants to navigable waters.

§ 422.36 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act for a source within the phosphate subcategory, which is a user of a publicly owned treatment works (and which would be

a new source subject to section 306 of the Act, if it were to discharge pollutants to the navigable waters), shall be the standard set forth in 40 CFR Part 128, except that process waste waters from this subcategory are not considered to be incompatible with publicly owned treatment works designed, constructed and operated to remove dissolved phosphate and, for the purpose of this section, § 128.133 of this title shall be amended to read as follows:

"In addition to the prohibitions set forth in 40 CFR 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works shall be the standard of performance for new sources specified in 40 CFR 422.35; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall, except in the case of standards providing for no discharge of pollutants, be correspondingly reduced in stringency for that pollutant."

[FR Doc.74-3496 Filed 2-19-74;8:45 am]

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 422]

APPLICATION OF EFFLUENT LIMITATIONS
GUIDELINES FOR EXISTING SOURCES
TO PRETREATMENT STANDARDS FOR
INCOMPATIBLE POLLUTANTS FOR THE
PHOSPHATE MANUFACTURING POINT
SOURCE CATEGORY

Notice of Proposed Rulemaking

Notice is hereby given pursuant to sections 301, 304 and 307(b) of the Federal Water Pollution Control Act. as amended (the Act); 33 U.S.C. 1251, 1311, 1314 and 1317(b); 86 Stat. 816 et seq.; Pub. L. 92-500, that the proposed regulation set forth below concerns the application of effluent limitations guidelines for existing sources to pretreatment standards for incompatible pollutants. The proposal will amend 40 CFR Part 422—Phosphate Manufacturing Point Source Category, establishing for each subcategory therein the extent of application of effluent limitations guidelines to existing sources which discharge to publicly owned treatment works. The regulation is intended to be complementary to the general regulation for pretreatment standards set forth at 40 CFR Part 128. The general regulation was proposed July 19, 1973 (38 FR 19236), and published in final form on November 8, 1973 (38 FR 30982)

The proposed regulation is also intended to supplement a final regulation being simultaneously promulgated by the Environmental Protection Agency (EPA or Agency) which provides effluent limitations guidelines for existing sources and standards of performance and pretreatment standards for new sources within the phosphate production subcategory, the pho phorous consuming subcategory and the phosphate subcategory of the phosphate manufacturing point source category. The latter regulation applies to the portion of a discharge which is directed to the navigable waters. The regulation proposed below applies to users of publicly owned treatment works which fall within the description of the point source category to which the guidelines and standards (40 CFR Part 422) promulgated simultaneously apply. However, the proposed regulation applies to the introduction of incompatible pollutants which are directed into a publicly owned treatment works, rather than to discharges of pollutants to navigable waters.

The general pretreatment standard divides pollutants discharged by users of publicly owned treatment works into two broad categories: "Compatible" and "incompatible." Compatible pollutants are generally not subject to pretreatment standards. (See 40 CFR 128.131 (Prohibited wastes) for requirements which may be applicable to compatible pollutants). Incompatible pollutants are subject to pretreatment standards as provided in 40 CFR 128.133, which provides as follows:

"In addition to the probabilions set forth in Section 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry not subject to Section 307(c) of the Act shall be, for a surces within the corresponding industrial o commercial category, that established by a promulgated effluent limitations guidelines defining best practicable control technology currently practicable control technology currently available pursuant to Sections 301(b) and 304(b) of the Act; provided that, if the publicly owned treatment works vaich receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant: And provided further. That when the eifluent limitations guidelines for each industry is promulgated, a separate provision will be proposed concerning the application of such guidelines to pretreatment."

The regulation proposed below is intended to implement that portion of § 128.133, above, requiring that a separate provision be made stating the application to pretreatment standards of effluent limitations guidelines based upon best practicable control technology currently available.

Questions were raised during the public comment period on the proposed general pretreatment standard (40 CFR Part 128) about the propriety of applying a standard based upon best practicable control technology currently available to all plants subject to pretreatment standards. In general, EPA believes the analysis supporting the effluent limitations guidelines is adequate to make a determination regarding the application of those standards to users of publicly owned treatment works. However, to ensure that those standards are appropriate in all cases. EPA now seeks additional comments focusing upon the application of effluent limitations guidelines to users of publicly owned treatment works.

, Sections 422.15, 422.25 and 422.35 of the proposed regulation for point sources within the phosphorus production subcategory, the phosphorus consuming subcategory and the phosphate subcategory (September 7, 1973; 38 FR 24470), contained the proposed pretreatment standard for new sources. The regulation promulgand simultaneously herewith contains §§ 422.16, 422.26 and 422.36 which state the applicability of standards of performance for purposes of pretreatment standard for new sources.

A preliminary Development Document was made available to the public at approximately the time of publication of the notice of proposed rulemaking and the final Development Document is now being published. The economic analysis report was made available at the time of proposal. Copies of the final Development Document and economic analysis report will continue to be maintained for inspection and copying during the comment period at the EPA Information Center, Room 227, West Tower, Waterside Mall, 401 M Street, SW., Washington, D.C. Copies will also be available for inspection at EPA regional offices and at

State water pollution control agency offices. Copies of the Development Document may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. Copies of the economic analysis report will be available for purchase through the National Technical Information Service, Springfield, Virginia 22151.

On June 14, 1973, the Agency pub-

On June 14, 1973, the Agency published procedures designed to insure that, when certain major standards, regulations, and guidelines are proposed, an explanation of their basis, purpose and environmental effects is made available to the public. (38 FR 15653). The procedures are applicable to major standards, regulations and guidelines which are proposed on or after December 31, 1973, and which either prescribe national standards of environmental quality or require national emission, effluent or performance standards or limitations.

The Agency determined to implement these procedures in order to insure that the public was provided with background information to assist it in commenting on the merits of a proposed action. In brief, the procedures call for the Agency to make public the information available to it delineating the major environmental effects of a proposed action, to discuss the pertinent nonenvironmental factors affecting the decision, and to explain the viable options available to it and the reasons for the option selected.

The procedures contemplate publication of this information in the FEDERAL REGISTER, where this is practicable. They provide, however, that where such publication is impracticable because of the length of these materials, the material may be made available in an alternate format.

The Development Document referred to above contains information available to the Agency concerning the major environmental effects of the regulation proposed below. The information includes: (1) The identification of pollutants present in waste waters resulting from the manufacture of phosphate, the characteristics of these pollutants, and the degree of pollutant reduction obtainable through implementation of the proposed standard; and (2) the anticipated effects on other aspects of the environment (including air, subsurface waters, soild waste disposal and land use, and of the treatment technologies available to meet the standard proposed.

The Development Document and the economic analysis report referred above also contain information available to the Agency regarding the estimated cost and energy consumption implications of those treatment technologies and the potential effects of those costs on the price and production of phosphate. The two reports exceed, in the aggregate, 100 pages in length and contain a substantial number of charts, diagrams and tables. It is clearly impracticable to publish the material contained in these documents in the FEDERAL REGISTER. To the extent possible, significant aspects of the material have been

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Dr. Martha Sager
Chairman, Effluent Standards
& Water Quality
Information Advisory Committee
Environmental Protection Agency
Room 821, Crystal Mall-Bldg. #2
Washington, D. C. 60460

Dear Dr. Sager:

Monsanto Company appreciates the opportunity to comment on the General Technologies Corporation draft contractors' report ("Development Decument for Effluent Guidelines and Standards of Performance for the Non-Fertilizer Phosphorus Chemicals Industry", dated June, 1973).

In this discussion, I would first like to have you consider with me some very serious questions I have about the intent and methodology described in the Development Document. Then, I would like to present several pre-liminary recommendations of my own.

Question: Are the zero-discharge limitations premature? Are they fair?

Are they based on fact?

The report recommends zero discharge of process water for six of eight products in the study.

Is this premature? It certainly is, if you assume (as we do) that zero discharge represents "best available technology". "Best available" is sought by 1983, according to Public Law 92-500. No mention of total climination or zero discharge is made about 1977 performance. The same Act, in Section 301b (1) and (2), states that total climination of pollutaints in a discharge may be required by 1983, if the technology is available. The Development Document's blanket requirement for zero discharge, to be achieved by 1977, must be considered as premature.

Tely 20, 1570 As not all values of the distance of end-point whole planes. The renor Stroll shotes -i ellicompilat assivery 1, the (17-79 (1) control and transment. soldings, los quantities (although not absolutely zero) and " R also points (in Section IN, Pages 15 and 16) to an elabe though to removal process involving lime treatment, clarafloreulation and direction as "achieving extremely low levels of total suspended and dissolved solids". Requiring the so kinds of operations to achieve zero discharge will mean abandonment or coally medification of very efficient end-point treatment. It will also mean a significant new capital investment for a very insignificant improvement. We would assume the companion economic impact study (now being undertaken by Archar D. Little & Co.) would reflect this. It is our understanding, however, that compliance costs have been prescribed in Supplement "A" of the total report (not a chased for comment), and is not to be further investigated. We also understand that the cost estimates per plant are in the 0-\$500M range. Compared to our preliminary estimates, this is an order of magnitude low. Are the zero discharge limitations technically realistic? We have enough concern to al least po the question. For example: In justifying zero precess discharge for phosphorus manufacture, the report states that the Tennessee Valley Authority has achieved total recycle of process streams other than phossy water. We have talked to TVA, and they tell us that their three process water streams (phossy water, precipitator dust sharry, and kiln scrubber systems) jointly discharge to the Tennessee River. The justification for more discharge for food-grade calcium phosphates is based on Monsanto's St. Louis operation. The report uses our rawwaste-load data, and then cuts the data in half (based on our plans to convert from wet scrubbers to bag collectors). On top of that, however, is applied sodium phosphate removal technology from our Trenton, Michigan plant. From that, a 0.5 ppm effluent (rather than the 50-100 ppm actual performance) is established. Finally, the report introduces further 1327

July 20, 1975

undemonstrated technology by supposing that polyrecrit flexculation data from EPA's municipal phosphorus removal test could as a be equival to this stream. The resulting hypethetical a beam would be good enough to recycle back into the food-grade process, the Document conduction.

Speaking from a very extensive manufacturing background, we at Lienaunto know that lime precipitation of calcium phosphates is highly questionable. We know the resulting chemistry would create insurmanutable quality problems. And we know that the cost of additional filtration, demineralizing, and sterilization necessary to re-use the water would be enough to economically drown the operation.

Other questions about the feasibility of zero discharge by 1977 arise in connection with the unique problems of multi-product plants, food-grade operations, product mix restraints, and process variations such as solution feed vs. slurry feed. Imagine the technical nightmare of trying to recycle the right material to the right process when the same plant produces several different products simultaneously, and at different times, and uses a multitude of raw materials showing up in the effluent stream.

These considerations were not reflected in the report.

Finally, no consideration was given to resultant air-quality or solid-waste problems. These include P2O5 and phosphine fumes from lime treatment and oxidation of phossy water, and disposal of high-moisture content sludge resulting from phosphate removal.

So to answer my own questions, I think the zero-process discharge recommendations are premature, unfair to "good-faith" manufacturers, and at least in some instances, not technically realistic. They also do not consider the differences among plant operations. They go far beyond the intent of Congress.

Question: Are the proposed pretreatment requirements realistic, or desirable in all cases?

The report recommends pretreatment standards which include total dissolved-solids limitations "the same as the applicable levels I, II, or
III Effluent Limitation Guidelines". In most cases, this would be zero!

By thus requiring total recycle, this provision would eliminate any industrial participation in Public Treatment Systems!

July 20, 1973

The propered standards allow remained a lettle proposed relief at 1950 point and maximum a concentrations of total phone is an fact 190g) of 30 pp.s. On a surcharge basis, several Messanto located a now pive manifely threatment systems to remove our suspended collete. Alles is obviously more economical to us. But it also recent as lower costs for mentally desystem customers, where these systems can attain economics of scale.

The 250 ppm limit also appears to contradict previous EPA guidelines. The EPA has repeatedly stated there will be no Federal pretreatment requirements for "compatible pollutants," such as suspended solids. The proposed limits on total pla phates also appear to be contradictory to the report's own requirement of zero total dissolved solids, and to EPA's stance that phosphate and its role as a nutrient should be considered a local problem, where across-the-board limits are unwise and unnecessary.

Question: What is a violation of a zero limitation?

Frankly, I can't answer this question, based on the report. There is no recognition of the variability of incoming water or of the limits of prescribed analytical techniques.

Question: Is there to be no allowable discharge of well water?

Apparently not, in most cases. On Page IX-8, it states that "Plant 159, intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities". This could mean that for a plant with a zero-process-discharge guideline, there is to be no discharge of any well water into a surface stream. This requirement is not justified in the report, and is not consistent with IX-2-2.0, which allows discharge of non-contact cooling water.

In addition, such a requirement would actually cause deterioration in surface water quality (in Plant 159 and other cases where well quality is superior to surface water). In cold-climate areas, it would cause severe operating problems. And it would deprive downstream users of accustomed and valuable water use rights.

We therefore recommend, and have recommended many times before, that the discharge of well water be considered on a case-by-case basis, and that any requirement recognize the relative quality of the well water and the surface stream involved.

RECOMMENDATIONS:

I would like to present some preliminary accommendations here:

- which allow continued use of existing effective, elaborate, and expensive water quality, programs short of zero discharge. Limits of 1 lb/ton T. S. S.; 10 lbs/ton T. D. S.; 0.4 lbs/ton fluoride; 0.35 lbs/ton total phosphate and zero elemental phosphorus are suggested.
- . That food-grade and multi-product phosphate salts plants be excluded from the proposed guidelines pending further study.
- . That pretreatment guidelines address only incompatible pollutants.
- . That discharge of well water be governed on a net effluent quantity basis unless local water quality requirements require more restrictive limitations.

IN CONCLUSION:

Monsanto has continually demonstrated its "good faith" in helping improver its water effluents. Realistic standards will pose no undue economic or technical obstacles to us. They will also prompt "laggers" to action. Unrealistic standards - as we feel the report presents - will produce innumerable delays as they are debated, argued, discussed, thereby deferred. This benefits no one.

We strongly urge reconsideration of the points discussed above. We stand ready to work with EPA, the Advisory Committee, and/or EPA's contractors to this end. More detailed page-by-page comments have been prepared and will be transmitted separately to EPA by August 1.

Again, we appreciate the opportunity to participate in this rule-making process.

M. L. Mullins
Manager
Environmental Protection

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO. 800 N. Lindbergh Boulevard St. Louis, Missouri 63166 Phone: (314) 694-1000

December 21, 1973

Mr. Elwood Martin
Effluent Guidelines Division
U.S. Environmental Protection Agency
Waterside Mall
Washington, D. C. 20460

Dear Woody:

This is to confirm our discussions in your office on December 20 regarding Monsanto cost data furnished EPA, General Technologies, Booz-Allen Associates, A. D. Little, Roy Weston, and ESWQIAC during the last 18 months. This was in response to criticism, expressed to the Department of Commerce, that Monsanto had not furnished useful cost data requested by EPA.

The following points were expressed on behalf of Monsanto:

- 1) Monsanto's policy regarding the guideline program has been one of total cooperation. To our knowledge, no information has ever been denied EPA. To the contrary, we have hosted nine plant visits, submitted extensive data, both directly to EPA and to its contractors, and testified on five occasions before ESWQIAC. For example, our review of the Phosphate and Inorganic Chemicals files in EPA's Public Information Offices indicates that no other single company has approached Monsanto's degree of participation.
- With specific regard to cost data relative to our Columbia, Tennessee and Trenton, Michigan plants, the data shown on Attachment A was submitted. In order to resolve the questions broached in our discussions, I have added explanatory notes as required.

Mr. Elwood Martin -2-Dec. 21, 1973 The only inquiry we ever received regarding this data was your phone call a week ago requesting more detail on the Trenton lime treatment plant. A preliminary response was mailed to you the same day, and more was forwarded directly from the plant on December 19. As to the comment that the \$700,000 cost submitted to the contractor appeared to be an effort to "pull EPA's leg," I can only suggest that such a statement without having seen the facility is unfair and I would like to repeat my invitation for you to visit this location and judge for yourself. 4) Monsanto encourages EPA to call or write us directly whenever any of our input presents any kind of a problem. The kind of inferences which were relayed to us by the Dept. of Commerce certainly got our attention, but I can assure you, resulted in transmittal of the same additional information a few days later than if we had been asked directly for the necessary clarification. I sincerely hope this information is of value as you make your final deliberations relative to the Phosphate Standards. We hope you will see fit to adopt guidelines - for phosphorus and food-grade phosphates in particular which are more defendable than "zero". We feel such limits, by reflecting the exemplary plant variations, would avoid the probable delays of legal challenge, the technical pitfalls of "zero", and would provide industry with a basis for timely action to meet attainable permit conditions. Again, please feel free to call on us if we can help. Very truly yours, M. L. Mullins Manager Environmental Protection MLM:ms Enc. cc: Dr. John B. Cox - Dept. of Commerce Mr. Allen Cywin - Environmental Prot'n. Mr. Walter Hunt -Mr. D. B. Hosmer - Monsanto Co. 1359

ATTACHMENT A

Trenton Lime Treatment Facility

The following cost data was included as Attachment "H" of Bryan Sevey's April 23, 1973 letter to General Technologies Corporation's Lee McCandless following the April 5 plant visit.

"The Effluent Treatment Plant operating costs are budgeted at \$358,000 in 1973. This includes chemicals, labor, utilities, depreciation, filter cake disposal and other items.

Capital investment for implementing Monsanto's Pollution Abatement Program was for:

Chemical and Cooling Water Sewer Separations
Recycling in the Spray Tower
The Effluent Treatment Plant

\$165,000
40,000
700,000*

\$905,000**

- * Part of the effluent treatment facilities were constructed using used or existing facilities and this figure represents, in part, an estimate of the true value of these facilities.
- ** This figure represents 1968 and 1969 dollars."

Added Comments

As was indicated, the \$700,000 figure represents an estimate of the present cost of the phosphate removal (lime treatment) plant. The actual cost to Monsanto in 1968-69 dollars was \$397,000 - however, the building, utilities, roads, settling ponds and some equipment were existing. The plant advises that because the construction was done by the plant, using substantial existing and used equipment, very little breakdown of project costs was done, except that the reaction portion (lime supply, reactors, agitators and instrumentation) cost \$126,000; and dewatering (thickener, vacuum filtration and ponds) cost \$271,000.

The contractor was also aware that the treatment facility, while serving only phosphate salt processes (8% Ammonium and 92% sodium), did not specifically serve sodium-tripoly phosphate. STP typically represents 50% of the 400 tons per day average phosphate salts production of the plant. We told the contractor that if differences in treatability exist between the various phosphates, we have not quantified them, and would design the plant the same way if it was to handle 400 tons/day of STP (or food-grade

1360

calcium phosphate). To adjust the estimate to reflect - for example - a 250 TPD calcium phosphate facility, one could factor by the 0.6 power as follows:

$$\left(\frac{250}{400}\right)^{0.6}$$
 x \$700,000 = \$528,000 1968-69 Dollars

One should probably also escallate approximately 10% for 1971 dollars (EPA's base) or better yet 30% to reflect 1975 dollars (which is probably about when compliance capital will be expended).

An allowance should also be provided for sewer separation and flow reduction steps necessary to reduce hydraulic loading. I still think \$1M is very probable!

Columbia, Tennessee Phosphorus Plant

This cost data was submitted to ESWQIAC on July 28, 1973. Since you apparently did not receive this input, I am attaching a copy. As indicated in Attachment "B", our estimate of the cost to achieve 'zero' for our Tennessee Phosphorus Plant is \$2.4M.

I believe the confusion which resulted here stemmed from interim guideline discussions last year (Oct. '72) when we stated that total evaporation of slag quenching water by duplicating our Soda Springs process was not economically feasible in that Tennessee furnace elevation is inadequate.

In the 7/28/73 estimate (which - although referenced in our 10/2/73 comments - was apparently never forwarded to you by ESWQIAC), a different, alternative was reflected - i.e. - ladle handling of slag to a remote air cooled slag bed. This approach, while still quite expensive, appeared superior to total evaporation of quench water, in that fluorine emissions are reduced by air cooling.

Monsento

MONSANTO INDUSTRIAL CHEMICALS CO. 800 N. Lindbergh Equipyard St. Louis, Missouri 63166 Phone: (314) 694-1000 #

July 28, 1973

Dr. Robert Grieves, Chairman Department of Chemical Engineering University of Kentucky Lexington, Kentucky 40500

Dear Sir:

This letter is in response to your request for more specific information re: Non-Fertilizer Phosphate Chemical Effluent Guidelines.

A brief summary of our comments and recommendations is offered below. In addition, Attachment A describes in detail the waste water practice of our Columbia, Tennessee plant (028 in the report). In that this is also the "representative plant" discussed in the Supplement A Cost Estimate, we have included our zero discharge cost estimate as attachment B. Our detailed critique of the contractor's report is Attachment C. Finally, Attachment D is the Columbia Plant portion of the voluminous Monsanto submission to the ESWQIAC Purdue University Workshop on Inorganic Chemicals on April 30 (prior to the Non-Fertilizer Phosphates being "split out").

Summary

The contractor recommends zero discharge guidelines for 6 of the 8 products covered. We can't argue that total recycle is probably a technical reality for some of these products. We submit, however, that it was not the intent of Congress to require existing plants with effective water quality control programs (short of zero discharge) to convert to total recycle by 1977. Taking another approach, E.P.T. was to be representative of the exemplary plants for each product - not the one best (ex: phosphorus) or a hypothetical composite of technology (ex: food-grade calcium phosphates).

Zero discharge guidelines for some products appear clearly reasonable specifically, for phosphoric acid and detergent grade sodium tripolyphosphateas long as these are single product, non-food-grade plants. The complexities
of multi-product and/or food-grade plants warrant further study which, we
believe, will result in guidelines which allow end-point treatment (ie: a treated
cilluent).

The contractor's pretreatment requirements of zero dissolved solids (for products with zero process discharge Level I direct discharge limits), 250 ppm suspended solids and 30 ppm PO_{.1} are unreasonable and contrary to the Act's intent of encouraging joint treatment.

Holding those discharging well-water responsible for the gross content would prohibit non-contact cooling water of higher quality than the receiving stream. This approach will have a serious impact on plants designed around cold, once-thru cooling water, on plants in areas subject to very cold Winters where total recycle involves special problems, and in areas where these discharges are a valuable commodity (see letter - Attachment "E" from Idaho resident who holds the first downstream claim to our discharge).

Recommendations:

- Adopt zero process discharge guidelines for phosphoric acid and detergent grade STPP. Exclude multi-product and food-grade sodium and calcium phosphate plants pending further study or, allow lime precipitation/vacuum filtration treatment to 0.25 #/ton PO₄ and T.S.S. Allow effluents of 1#/ton T.S.S. (5ppm), 0.4#/ton fluoride and PO₄ and zero elemental P₄ from phosphorus plants. These levels would allow continued operation of plants 628 and 159 which, according to the contractor's report "achieve very high (97-99%+) removal". Attachment "A" data supports this position. As for the remaining products, we don't make P₂O₅; expect problems attaining level I for PCl₃ and POCl₃ only re: elimination of Cr₆ from utility blowdown streams; and aren't convinced collection of P₂S₅ casting fumes without an effluent is demonstrated.
- Limit pretreatment guidelines to pH, temperature, toxics, etc. (ie: delete T.S.S., T.D.S. and phosphates) which are not incompatible with public treatment.
- Exclude T. D. S. from effluent guidelines due to questionable water quality significance and lack of practical control technology. This step was taken by EPA last Fall relative to the interim guidelines and is still appropriate.
- Delete "gross responsibility" approach to use of well-water. Water
 quality priority over effluent limitations will avoid such a decision from
 compromising the effectiveness of the Act.
- Exclude ore washing from the scope of these guidelines per contractor's recommendation.

That's about it. The M.C.A. Committee handling Inorganic and Non-Fertilizer Phosphates met with the Advisory Committee Friday and conveyed additional comments which are to be mailed to you next week. Please don't hesitate to call me at 314-694-2648 if we can answer any questions or provide any additional information.

-3-

Very truly yours,

M. L. Mullins, Manager Environmental Protection

cc: Dr. Martha Sager (9)

Notes:

Some further definition re: how zero discharge limits would be enforced is needed to cope with analytical limits, variations in source water malysis, etc. Provision for disposing of contained spills, leaks, contaminated material, and similar off-grade materials is also needed for those cases where working these materials back into the process is not possible.

²This method is recommended vs: settling ponds due to the greatly reduced property requirements.

bcc:

- D. B. Hosmer
- J. T. Garrett
- P. F. Cunningham
- J. E. Feltham
- G. DePagter Columbia
- W. Perdue -
- K. Lott Soda Springs
- J. Reeve "

ZEED DISCHADRE COST ESTIMATE PLANT DZZ

LASTALL LADLE HOMELING TO ALLOW AIR COSLINGS

SLAG CRECYCLE OF SLAG COOLING LUATER LUNGLID

RESULT IN LIMITCOPPORTED HE CONTESTIONS)

CADITAL COST 2.000,000

2. INISTALL HYDRO, LIME SLAKER, LINDERFORD PUND PUNIPS & PIPING TO ALLDED RECYCLING MODULE HANDLING AND FURNIACE STOCKING DUCT COLLECTOR SCRUBBING LIDEDIC WID SCALING - 1000 EPN

Carrier Cost 350,000

3. INSTALL PUNIT SUMME & INT-LINE PH CONTROL COMPRENT TO ALLOW BECKEING COLF DIST COMPETION SCHUDICE CONTRACT.

CAPITAL COST \$50,000

Torne Cost 2,400.000

THIS WOULD BE LESS EXPENSIONS THAN GIES BASIS OF "CONNECTIME EFFECTIONS NOW CONTROLS."

Arthur D. Little, Inc. ACORN PARK - CAMBRIDGE MASSACHUSETTS 02140 - (617) 864-5770

August 15, 1973

Mr. John Savage Environmental Protection Agency Waterside Mall 401 M Street, S.W. Room 3009 (Low Mall) Washington, D.C.

Dear John:

Enclosed is a brief memorandum outlining some preliminary comments of several producers with whom we have talked, concerning the GTC non-fertilizer phosphate guidelines. We have not actively solicited their comments, so probably will not be receiving much in addition to this.

Very sincerely yours,

George C. Sweeney

GCS/s1

Enc.

1588

To: EPA

Case: 75907 Date: August 14, 1973 Page:1

Subject: Industry Comments on GTC Report, Including Supplement A, "Cost Information for Mater-Borne Martes in the Mon-Vertilizer Phosphorous Chemicals Industry"

Following are the comments of acceral producers after having examined the draft report and the draft Supplement A presented by GTC.

Producer A

- Incorrect that the industry has in general the technical capability to achieve zero discharge.
- Concerned about how they (GTC) treat water treatment chemicals. The water de-ionizers are regenerated with sulphuric acid and caustic soda. While the material goes out as a neutral solution, it is very concentrated with salts.

Producer B

- Of the opinion that the only way zero discharge can be achieved for the phosphates is by final evaporation. The real cost of total evaporation is estimated to be 2 to 3 times that estimated in the base report of GTC.
- For the general range of 450 gallons per minute, estimates that the cost of evaporation to be at least \$10.00 per thousand gallons as opposed to \$5.50 \$6.00 per thousand gallons estimated by GTC. The higher fuel costs are the principal reason.
- Commented that EPA regulation ignored the pollution to underground water from unlined ponds or buried solids.
- In the case of STPP, have real questions about the practicality of using dry dust collectors with sodium phosphates on humid days. The GTC costs make no provision for wash out of clogged filters which may be necessary 2 3 times per yeek. Such washings generate too much water for return to process.
- In the case of anhydrous derivatives, question the feasibility of returning the water from the scrubbers to the scrubbing operation and thus continuing to concentrate. This can only be carried so far, and then scrubbing water must be bled off. Instead of taking sludge to land fill, it will be necessary to move a slurry. In other words, the lime treatment and settling tanks will not provide a true sludge and evaporation is necessary. Also questioned whether any cost for handling of sludge are included in the cost of CTC.

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| | | | | | | |

EPA To:

Case: 75907

Date: August 14, 1973 Page: 2

Subject: Industry Comments on GTC Report

Producer C

- Felt that GC costs in general were extremely low. Surmized that GC had included only equipment costs, and had neglected erection costs, land acquisition, etc. For example, in one lime treatment and filtration process for calcium phosphates, GTC had estimated about \$33,000 in capital costs. Their own estimates were in the neighborhood of \$700,000.
- Strongly questioned their recommendations for zero discharge. The technology had definitely not been proven for a number of their plants.
- They simply did not know how to achieve zero discharge at the present time for certain products.

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Bldg./Room. 35/292 Ext. 2776

Arthur D. Little, Inc. ACCENTABLE - CAMBRIDGE MASSACHUSETTS 02140 - 1617, 864 5770

August 3, 1973

Mr. John Savage Environmental Protection Agency Waterside Mall 401 M Street, S.W. Room 3009 (Low Mall) Washington, D.C.

Dear John:

I have enclosed with this letter a brief memorandum outlining some initial and informal reactions to the guidelines prepared by the GTC relating both to cost and technology. These reflect primarily our own engineers' comments. In contact with industry we have received a number of additional reactions. Some were highly critical while others felt that certain of the guideline proposals were reasonable and achievable.

Very sincerely yours,

George C. Sweeney

John - the deplicate copy in con the I'm south week you was your mignist didn't much you was south your might commont shorth - George Livering.

1591

distinct control and treatment technology,

To: EPA

Case: 75907 Date: August 3, 1973

Subject: Comments on Industrial Prosphate Guidelines

Page: 1

Phosphorus

The cold weather encountered in the area where the western plants are located creates substantial problems in the operation of settling ponds and may also require the use of buried pipe heated pumps, etc.

Settling ponds located in areas of high rainfall as for example might be encountered in Tennessee and Florida, would entail some runoif from the settling ponds during heavy rains.

Phosphoric Acid

There may be some problems associated with the disposal of the arsenic sludge.

Phosphorus Pentoxide

Total recycle is probably not practicable, some purge will be needed since soluble impurities in water makeup and introduced with lime will eventually build up because of evaporation in scrubber. They will thus scale and plug equipment requiring a shutdown and washout.

Phosphorus Pentasulfide

Total recycle probably cannot be carried out or approached in present equipment. The sulfate-sulfite-lime system, once concentrations build up, requires special scrubbing and fluid handling techniques to keep the severe scaling under reasonable control. The problem in lime scrubbing of flue gas illustrates this point.

Phosphorus Clorides

The calcium chloride can only be concentrated to the hexahydrate which melts at 30 C and is hygroscopic to the degree the crystals (below 30 C) will absorb water and dissolve. Thus, the evaporators will have a liquid effluent.

STPP

Most plants make several types of condensed phosphates in the same equipment which complicates the simplified picture presented by GTC. The products and grades of the same product are not interchangeable and equipment must be washed out for product changes.

Food Grade Phosphates

It seems highly improbable that product specifications can be maintained on total recycle since impurities entering with makeup water and the raw materials will build up in concentration. Some purge would be necessary

1592

Arthur D Little Inc

ADL-115-7/2

Case: 75907

Date: August 3

Page:

Subject: Comments on Industrial Prosphate Guidel nes

to remove these from the mother liquor.

Overall

The cost of equipment and treatment techniques proposed by GTC has not been reviewed. Our feedback from industry indicates that they believe many of the cost figures presented are substantially understated.

The steam costs seem very low (\$.70 per thousand pounds). The cost of steam is likely to be at least \$1.50 or more.

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1593 Arthur D'Little Inc

ADL-115-772

Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the

PHOSPHORUS DERIVED CHEMICALS

Segment of the Phosphate Manufacturing Point Source Category

JANUARY 1974



U.S. ENVIRONMENTAL PROTECTION AGENCY
Wasnington, D.C. 20460

DEVELOPMENT DOCUMENT

for

EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

PHOSPHORUS DERIVED CHEMICALS SEGMENT OF THE

PHOSPHATE MANUFACTURING

POINT SOURCE CATEGORY

Russell E. Train Administrator

Robert L. Sansom Assistant Administrator for Air and Water Program



Allen Cywin Director, Effluent Guidelines Division

> Elwood E. Martin Project Officer

> > January 1974

Office of Air and Water Programs
U.S. Environmental Protection Agency
Washington, D.C. 20460

1645

ABSTRACT

P2S5, and PCI5) is essentially by the direct the

A study was made of the phosphate manufacturing point source category by the General Technologies Corporation for the Environmental Protection Agency for the purpose of developing effluent limitations guidelines, Federal standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act Amendments of 1972.

For the purpose of this study, the phosphate manufacturing industry was defined as the manufacture of the following chemicals: Phosphorus (and by-product ferrophosphorus), phosphoric acid (dry process only), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, phosphorus oxychloride, sodium tripolyphosphate and the calcium phosphates.

Effluent limitations guidelines were developed as a result of this study, defining the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977, and July 1, 1983, respectively. The standards of performance for new sources were also defined.

The best practicable control technology currently available allows a discharge after suitable treatment for the manufacture of phosphorus (and ferrophosphorus), phosphorus trichloride, phosphorus oxychloride and food grade calcium phosphate. The 1977 limitations prohibit discharge of process waste water pollutants for the manufacture of the remaining chemicals.

Application of the best available technology economically achievable and best demonstrated technology would enable all the manufacturing operations for the three subcategories to achieve no discharge of waste water pollutants.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the phosphate manufacturing point source category was divided into the phosphorus production, the phosphorus consuming, and the phosphate subcategories.

Phosphorus and phosphoric acid (furnace acid) production were included in this study because they are necessary prerequisites to phosphate synthesis. It is also appropriate from a technical standpoint to include these chemicals in this study rather than in the inorganic chemical point source category. Other phosphorus consuming chemicals such as PCl3 and P2O5 were included for the same reasons. Processes that manufacture phosphates as fertilizers are regulated by the fertilizer manufacturing regulations.

The phosphorus-production subcategory of the industry is characterized by large quantities of raw process wastes, including highly deleterious phossy water and highly-acidic scrubber and quenching waste waters, both containing large quantities of fluorides, other dissolved solids, and suspended solids. Through a combination of in-process controls and end-of-process treatment, several plants within this segment have achieved zero discharge of other process waste waters, and one has achieved zero discharge of other process waste waters, and one has achieved zero discharge of any waste water during normal periods of rainfall. Plants now demonstrate abatement practices resulting in 97 percent or greater reduction in the raw waste load before discharge, and the total recycle of process water without any discharge has been demonstrated using the best practicable control technology.

The phosphorus-consuming subcategory of the industry is characterized by the absence of direct process waste water; the chemicals produced are readily hydrolyzed so that the processes are essentially dry. However, just because the products are readily hydrolyzed, water is universally used for air pollution abatement scrubbing of tail gases, for periodic cleaning of reaction vessels, and for the general washing of shipped containers, all resulting in acidic waste waters. In addition, water is used in protecting and transferring the raw material, elemental phosphorus, and phossy water is therefore a raw waste from this segment. Except for the manufacture of dry-process phosphoric acid (where in-process control has been demonstrated to achieve zero discharge of aqueous wastes), this segment yet achieved sufficient reduction of effluents. application, however, of currently available technology is shown by this study to permit total recycle of waste waters (and so zero discharge) for the manufacture of P205 and P2S5, and to achieve the neutralization and removal of most suspended solids before discharge for the manufacture of PCl3 and POCl3.

latter two processes are more expensive but still economically achievable technologies and are available for treating the chlorides so as to achieve zero discharge.

The phosphate segment of the industry, i.e., the group of chemicals manufactured from phosphoric acid, is characterized by acids and by finely-divided solids in the raw aqueous wastes. Several plants have already achieved zero discharge by in-process controls and by end-of-process treatment; and this study shows how this segment may achieve zero discharge by applying currently available practicable technology. Outside contamination of the process waste water resulting from the manufacture of food grade calcium phosphate may prevent its reuse at existing plants, and a discharge after suitable treatment has been allowed.

The general conclusion reached is that the industry has already solved its most serious raw waste problem; that is, the abatement of water pollution from phosphorus-producing facilities. The remainder of the industry, made up of much smaller-volume plants, has lagged behind in elluent reduction, but technology is available to make the entire industry notable.

SECTION II

shoonhate rock is carefully pretreated by drying,

RECOMMENDATIONS

The recommended effluent limitations guidelines based on best practicable control technology currently available are no discharge of process waste water pollutants to navigable waters for the manufacture of the following chemicals:

Phosphorus Consuming Subcategory
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphate Production Subcategory
Sodium Tripolyphosphate
Calcium Phosphates (Animal Feed Grade)

The recommended effluent limitations for this technology for phosphorus (and ferrophosphorus), phosphorous trichloride, phosphorous oxychloride and food grade calcium phosphate are given in Table 1.

The above guidelines apply to the maximum average of daily values for any period of 30 consecutive days. The maximum for any one day is twice the consecutive 30 day average value. The pH limitation must be met at all times. It is recommended that noncontact cooling water be allowed to be discharged. Effluent limitations for this waste stream are expected to be covered in future studies. For the purposes of this report, process water is defined as any water that comes into direct contact with any raw material, intermediate product, by-product, or gas or liquid that has accumulated such constituents.

The recommended effluent limitations guidelines based on best available technology economically achievable is no discharge of process waste water pollutants for the manufacture of the following chemicals:

Phosphorus Consuming Subcategory
Phosphorus (and Ferrophosphorus)

Phosphorus Consuming Subcategory

Phosphoric Acid (Dry Process)

Phosphorus Pentoxide Phosphorus Pentasulfide Phosphorus Trichloride Phosphorus Oxychloride

Phosphate Subcategory

Sodium Tripolyphosphate

Calcium Phosphates (Food Grade)

Calcium Phosphates (Animal Feed Grade)

The recommended new source performance standards are the same as the above recommended best available technology economically achievable.

TABLE 1.

Recommended Best Practicable Control Technology Currently Available for the Manufacture of Phosphorus (and Ferrophoshorus), Phosphorus Trichloride, Phosphorus Oxychloride and Food Grade Calcium Phosphate. (Process Water)

The recommended effluent limitations guidelines based on best practicable control technology currently available for process water for the manufacture of PCl3 and POCl3 are:

Average of daily values for thirty consecutive days shall not exceed

| | | Phosphorus and Ferrophosphorus | Phosphorus <u>Trichloride</u> | Phosphorus Oxychloride | Food Grade Calcium Phosphate |
|---------------------------------|---------------------------|--------------------------------------|----------------------------------|---------------------------|------------------------------------|
| Total Sus Nonfilte Solids | pended rable kg/kkg | 0.5 | 0.7 | 0.15 | 0.06 |
| Total Pho | sphorus kg/kkg | | 0.8 | 0.17 | 0.03 |
| Fluoride Arsenic | kg/kkg kg/kkg | 0.05 | 0.00005 6.0-9.0 | 6.0-9.0 | 6.0-9.0 |

to either event, some of the fluorides from the

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304 (b) of the Act. Section 306 of the Act requires the achievement by new sources of a standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be available achievable through the application of the best demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the phosphate manufacturing point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention to establish, under Section 306, standards of performance applicable to new sources within the phosphate manufacturing source category.

SUMMARY OF DEVELOPMENT METHODS

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the promulgation of effluent standards from industrial sources. A systematic approach to the achievement of the required guidelines and standards includes the following:

(a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and

standards need to be set:

(b) Characterization of the waste loads resulting from discharge within industrial categories and subcategories;

(c) Identification of the range of control and treatment technology within each industrial category and subcategory:

(d) Identification of those plants having the best practical

technology currently available (notable plants); and

(e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable current

technology.

This report describes the results obtained from application of the above approach to the phosphate manufacturing industry, defined for the purpose of this study as the following list of products:

Elemental Phosphorus and Ferrophosphorus
Dry-Process Phosphoric Acid
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphorus Trichloride
Phosphorus Oxychloride
Sodium Tripolyphosphate
Calcium Phosphates (Non-Fertilizer)

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. point source category was first subcategorized for the purpose of whether separate limitations and standards are determining appropriate for different segments within a point source cate-Such subcategorization was based on raw material used, gory. product produced, manufacturing process employed, and other fac-The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant, and (2) the constituents (including thermal) of all waste waters including toxic constituents which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies which are existent or capable of being designed for each subcategory. also included an identification in terms of the number of constituents (including thermal). The chemical, physical, and biological characteristics of pollutants of the effluent level resulting from the application of each of the treatment and control technologies and the required implementation time were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies on other pollution problems, including air, solid waste, radiation, were also identified. The energy requirement of each of the control and treatment technologies was identified as well as the cost of the application of those technologies.

The information as outlined above was then evaluated to determine what levels of technology constituted the best practicable control technology currently available, the "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying the technologies, various These included the total cost of factors were considered. application of technology in relation to the effluent reduction benefits to be achieved from the application, the age of equipment and facilities involved, the process employed, the non-water quality engineering aspects, process changes, environmental impact (including energy requirements), and other factors.

The data for identification and analysis were derived from a number of sources. These sources included EPA research information, published literature, previous EPA technical guidance for inorganic chemicals, alkali and chlorine industries, qualified technical consultation, and on-site visits and interviews at notable manufacturing plants throughout the United States. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII of this document. Five companies in the phosphate manufacturing industry were contacted. A breakdown of the data base is listed below:

Number of Plants in Data Base Chemical Literature Inspected Sampled Permit Application 3 2* 2 1* H3P04 1 1 1 P205 2 2 P2S5 2 PC13 2 POCÎ3 Na5P301C

*Includes verification of plants with no discharge.

In addition much information was obtained from plant personnel at the time of plant inspections, plant sampling, and company discussions.

GENERAL DESCRIPTION OF THE INDUSTRY

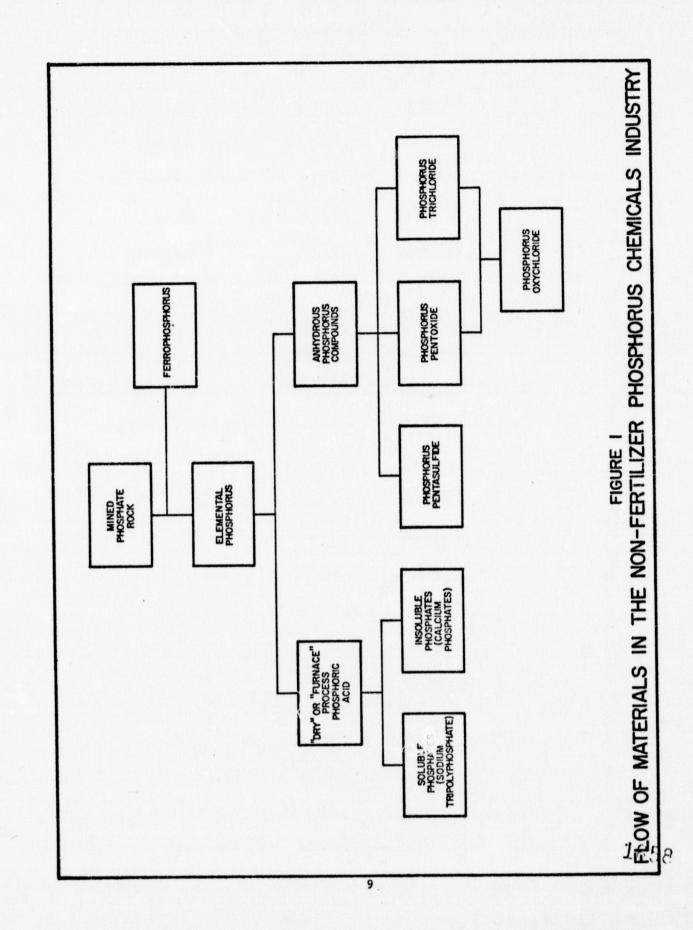
(Food Grade)
(Feed Grade)

The industry covered by this document is the phosphate manufacturing point source category. It is more descriptively termed the nonfertilizer phosphorus industry. The following chemicals covered by SIC 2819 were studied:

phosphorus
ferrophosphorus
phosphoric acid (dry process)
phosphorus pentoxide
phosphorus pentasulfide
phosphorus trichloride
phosphorus oxychloride
sodium tripolyphosphate
calcium phosphates (food grade)
calcium phosphates (animal feed grade)

Other phosphorus and phosphate chemicals are expected to be covered at a later time.

The flow of materials in the phosphate manufacturing industry is depicted in Figure 1. This industry is almost entirely based on the production of elemental phosphorus from mined phosphate rock. The economics have dictated that the phosphorus production facilities be located at the sources of the raw material, which are in three areas in the United States: Tennessee, the Idaho-Montana area, and Florida. The key in-plant siting decision is the relative weights of phosphate rock, elemental phosphorus and phosphoric acid (about 10:1:4). Hence, the rock is processed close to the mine and the acid is produced close to its consumption point; the relatively low-weight elemental phosphorus is almost universally the form shipped from place to place.



Ferrophosphorus, widely used in the metallurgical industries, is a direct by-product of the phosphorus production process, since most furnace-grade phosphate rock contains 2 to 6 percent iron oxide.

Over 87 percent of the elemental phosphorus is used to manufacture high-grade phosphoric acid by the furnace or "dry" process as opposed to the wet process which coverts phosphate rock directly into phosphoric acid. This lower-grade wet process acid is almost exclusively used in the fertilizer industry and is separately discussed in that report. The remainder of the elemental phosphorus is either marketed directly or converted to chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. These chemicals are chiefly used in synthesis in the organic chemicals industry.

Much of the furnace-grade phosphoric acid is directly marketed, largely to the food industry and to the high-grade fertilizer industry. Phosphoric acid is also used to manufacture two basic classes of phosphates: water-soluble phosphates used in detergents and for water treatment, typified by sodium tripolyphosphate, and water-insoluble phosphates which are used in animal feeds and in foods, typified by the calcium phosphates.

The processes involved in the non-fertilizer phosphorus chemicals industry are very briefly as follows:

Elemental phosphorus and ferrophosphorus are manufactured by the reduction of phosphate rock by coke in very large electric furnaces, using silica as a flux. Very large quantities of water are circulated for cooling the very hot equipment, for cooling and granulating the slag, and for condensing the phosphorus vapor from Since water is both non-reactive and furnace. immiscible with liquid phosphorus, water is used extensively in direct contact with phosphorus for heat transfer, for materials transfer, for protection from the atmosphere, and for purification. This study is concerned with manufacturing operations subsequent to receiving washed phosphate ores at the phosphorus production facility. Ore benefication is commonly but not exclusively conducted at a separate off-site location. The huge waste load from benefication, 7500 kg of gangue per kkg of phosphorus eventually produced, warrants a separate study as a segment of the mining industry.

Phosphoric acid manufactured by the "dry" or furnace process consists of the burning of liquid phosphorus in air, the subsequent quenching and hydrolysis of the P2O5 vapor, and the collection of the phosphoric acid mists. The operation uses cooling water, and process water is consumed in making the aqueous acid. Solid wastes may be generated should a plant later purify the acid.

The product acid is nure but for the manufacture of food grade

The manufacture of the anhydrous phosphorus chemicals (P2O5, P2S5, and PCl3) is essentially by the direct union of phosphorus with the corresponding element. Phosphorus oxychloride, PCl3, is manufactured from PCl3 and air or from PCl3, P2O5, and chlorine. Water use is limited to cooling water, to water for transferring elemental phosphorus, to scrubber water, and to wash water for reaction vessels and shipping containers.

Sodium tripolyphosphate is manufactured by the neutralization of phosphoric acid with the appropriate proportions of caustic soda and soda ash in mix tanks. The resulting mixture of mono- and di-sodium phosphates is dried and the crystals calcined to produce the tripolyphosphate.

The calcium phosphates are similarly made by the neutralization of phosphoric acid with lime. The amount and type of lime used and the amount of water in the process determine whether anhydrous monocalcium phosphate, monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, or tricalcium phosphate is the final product. Table 2 lists production tonnages for these chemicals as reported by the U.S. Bureau of Census. As seen from this table the industry is relatively small in relation to numbers of plants.

Table 3 lists the current selling prices of the chemicals within this industry. Table 4 lists the producers of phosphate products.

TABLE 2. U.S. Production of Phosphates

| Chemicals | Metric Tons | Short Tons | Number of Plants |
|-------------------------|-------------|-------------|---------------------|
| Phosphorus | 495,000 | 545,000 | 10 |
| Ferrophosphorus | 110,000* | 121,000* | |
| Phosphoric Acid | 1,640,000** | 1,810,000** | 25 |
| (Furnace Process) | | | |
| Phosphorus Pentoxide | (withheld) | (withheld) | (withheld) |
| Phosphorus Pentasulfide | 54,000 | 59,000 | 5 |
| Phosphorus Trichloride | 50,000 | 55,000 | 4 |
| Phosphorus Oxychloride | 28,000 | 31,000 | 4 |
| Sodium Tripolyphosphate | 945,000 | 1,040,000 | 17 |
| Calcium Phosphates | 536,000 | 592,000 | 7 |

^{*}Independently estimated. (2)

**Estimated as 87 percent of phosphorus consumption, using
90 percent conversion, and stated as acid of 54 percent P2O5. The total production of phosphoric acid both wet and dry was 5,650,000 kkg (6,240,000 short tons).

TABLE 3. Current Selling Prices of Phosphorus Chemicals Source: Chemical Marketing Reporter, June 25, 1973

| | | SELLING F | |
|---------------------------|------------------------|---------------|--------------|
| CHEMI CAL | GRADE | \$/Metric Ton | \$/Short Ton |
| White Phosphorus | | 419 | 380 |
| Phosphoric Acid (Furnace) | 75% Commercial & Feed | 164 | 149 |
| | 80% Commercial & Feed | 176 | 160 |
| | 85% National Formulary | 194 | 176 |
| Phosphorus Pentoxide | | 441 | 400 |
| Phosphorus Pentasulfide | | 299 | 271 |
| Phosphorus Trichloride | | 292 | 265 |
| Phosphorus Oxychloride | | 270 | 245 |
| Sodium Tripolyphosphate | Technical Food | 179 270 | 162 245 |
| Monocalcium Phosphate | Anhydrous Food | 314 | 285 |
| Dicalcium Phosphate | U.S.P Food Feed | 286 82 | 259 74 |
| Tricalcium Phosphate | NF Precip. | 315 | 286 |

TABLE 4

| | Phosphorens | Phosphorous Pentoxide | Phosphorous Trichloride | Phosphorous Oxychloride | Phosphorous Pentasulfide | Furnace | Sodium Tripolyphosphate | Feedstock Dicalcium Phosphate | Technical Calcium Phosphate |
|----------------------------------|-------------|--------------------------|----------------------------|----------------------------|-----------------------------|---------|----------------------------|-------------------------------------|-----------------------------------|
| | | | | | | | | | |
| Holmes Company | 0 | | | | | | | | |
| FMC Corporation | 0 | | 0 | 0 | | 0 | • | | |
| Nobil Corporation | 6 | | 0 | | | 0 | 0 | | , |
| Monsante Company | 0 | | • | 0 | • | • | • | | c |
| Occidental Petroleum Corp. | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| Stauffer Chemical | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 0 |
| TVA | 0 | | | | | 6 | , | | |
| Olin Corporation | | | | | | | 0 | 1 | |
| Goodpasture, Inc. | | | | | | • | | | |
| American Cyantd Co. | | | | | | | | 0 | |
| Borden, Inc. | | | | | | | | 0 | |
| Eastman Kodak Co. | | | | | | | | | 0 |
| Farmland Industries | | | | | | | | 0 | |
| Int'l. Minerals & Chemical Corp. | Corp. | | | | | | | 0 | |
| Knox Gelatine, Inc | | | | | | | | | 0 |
| Richardson-Merrell, Inc. | | | | | | | | | • |

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DETAILED PROCESS DESCRIPTIONS

The following is a description of each process in this industry. Process flow diagrams are included. In generating the following descriptions, emphasis has been placed on process features which generate aqueous wastes. The details of the waste stream character, however, have been left for discussion in Section V.

Much of the process data in this section were acquired by discussions with industry personnel and by observation of existing A large body of data also exists in the published literature, and was used extensively in the following discussion. Of particular usefulness were the publications of Beveridge and Hill; (4) Barber, (5,6) Barber and Farr; (7) LeMay and Metcalf (8) of The Tennessee Valley Authority, which supplied very specific operating details of TVA's facilities; Ellwood; (9) and Bryant, Holloway and Silber (10) of the Mobil Chemical Company. Standard reference books such as Faith, Keyes and Clark, (11) kirk and Othmer, (12) and Shreve, (13) were also useful.

THE PHOSPHORUS PRODUCTION SEGMENT

Phosphorus is manufactured by the reduction of mined phosphate rock by coke in an electric furnace, with silica used as a flux. Slag, ferrophosphorus (from iron in the phosphate rock), and carbon monoxide are reaction by-products. The simplified overall reaction may be written:

 $2Ca_{\frac{3}{2}}(PO_{\frac{4}{2}})_{\frac{2}{2}} + 10 C + 6SiO_{\frac{2}{2}} + 1500^{\circ}C P_{\frac{4}{2}} + 10 CO + 6CaSiO_{\frac{3}{2}}$

Products

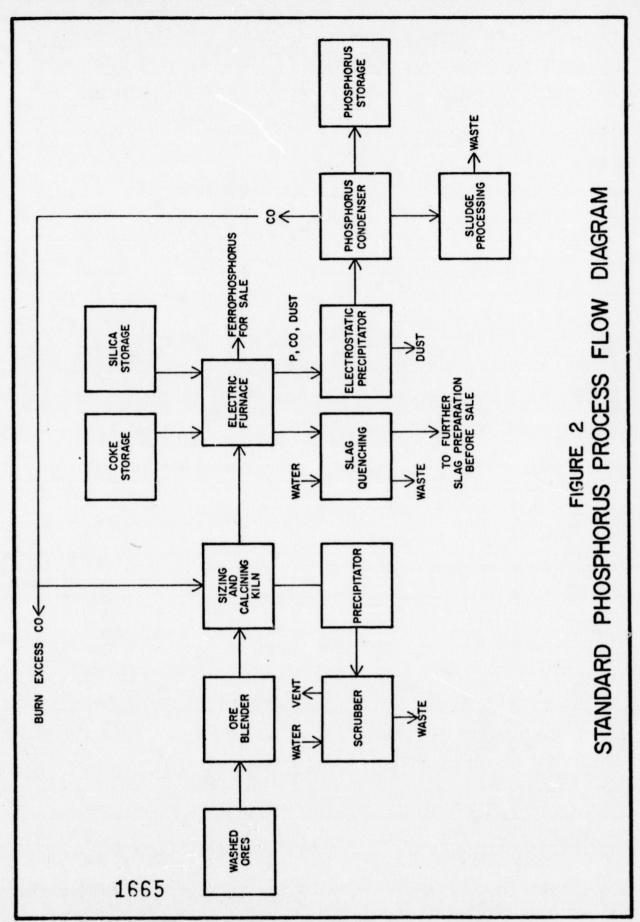
A typical material balance for the process is:

| Raw Mater: | <u>ials</u> | Products | |
|----------------------------------|------------------------|----------------------------------------------------------|------------------------------|
| Phosphate Rock Silica Coke | 10.0 kkg 1.5 1.5 | Phosphorus Ferrophosphorus Slag Carbon Monoxide | 1.0 kkg 0.3 8.9 2.8 |
| Total | <u>13.0</u> kkg | Total | 13.0 kkg |

The electrical power consumption is approximately 15,400 KWH/kkg (14,000 KWH/ton) of phosphorus produced; part of this supplies the endothermic heat of reaction of 6,200 KWH/kkg of P4.

The standard process, as pictured in Figure 2, consists of three basic parts: phosphate rock preparation, smelting in the electric furnace, and recovery of phosphorus.

Phosphate rock ores are first blended so that the furnace feel is of uniform composition. The silica composition is important since the overall furnace feed must have a SiO2/CaO ratio close



to the eutectic composition for desired slag flow properties. The blended phosphate rock is carefully pretreated by drying, by agglomerating the particles, and by heat treatment.

After the raw phosphate rock is dried, sizing or agglomeration is pelletizing, briquetting, flaking, by accomplished "nodulizing," and pre-formed agglomerates are then calcined in a The nodulizing operation performs simultaneous rotary kiln. agglomeration and calcining by heating the rock to its incipient fusion point, with subsequent crushing, sizing, and recycling of Sizing promotes the even distribution of gas flow within the furnace and results in more efficient heat transfer and lower The size of the furnaces has dramatically total energy costs. accentuating the needs increased in recent years, stoichiometric balance and thermal homogeneity within the charge (or "burden"). Heat treatment or calcining of the feed increases the strength and hardness of the particles, preventing large quantities of fines from being formed by attrition.

The calcining, at 1000 to 1400°C, also liberates water of hydration, organics, carbon dioxide, and fluorine at a much lower energy cost than would be required in the subsequent electric furnace operation. Since 25 percent of the manufacturing costs of phosphorus are for electric power, considerable effort is made to conserve this power. Moreover, by-product carbon monoxide from the smelting operation is available as a source of auxiliary energy.

The sizing and calcining operations are sources of dust and of fluorine fumes. The dust may be electrostatically precipitated, and the gases are scrubbed with water, removing fluorine as HF and H2SiF6. The dry dusts collected are normally recycled to the

nodulizing operation. The burden of treated phosphate rock, coke, and sand is charged to the furnace by incrementally adding weighed quantities of each of the three materials to a common belt conveyor. The furnace itself has a carbon crucible, carbon-lined steel sidewalls and a two-foot-thick self-supporting cast concrete roof. In an effort to eliminate periodic roof replacement due to excessive cracking of the concrete, some newer furnaces have anti-magnetic (to avoid induction heating) stainless steel roof structures. Penetrations in the furnace are for feed chutes, for carbon electrodes, for tap holes, for slag (upper liquid layer), for ferrophosphorus (lower liquid layer), and for exhaust gases.

Electric furnaces for phosphorus production have been dramatically increasing in size to achieve operating economies: Phosphorus Oxychiciade

| | Size of Lard | in Operation | |
|-------------|--------------|--------------|-----------|
| <u>Year</u> | Megawatts | kkg/Year | Tons/Year |
| 1950 | 25 | 13,600 | 15,000 |
| 1960 | 50 | 27,200 | 30,000 |
| 1970 | 65 | 36,300 | 40,000 |

The smallest furnaces produce 9,100 kkg (10,000 tons) of phosphorus per year.

An appreciation of the physical size may be attained from the fact that the largest carbon electrodes used are 1.5 to 1.8 meters (5 to 6 feet) in diameter and carry 50,000 amperes each.

The furnace is extensively water-cooled. Cooling water is used for the electrical transformer, for the furnace shell, for the crucible bottom, for the fume hood, for the tapholes, and for electrode joints. Newer furnaces use telescoping water seals on furnace electrodes; and for TVA-type furnaces with rotating crucibles a water seal is provided between the crucible and the stationary roof.

The 2 to 6 percent Fe203 in the furnace-grade phosphate rock is reduced, with the iron recovered as the ferrophosphorus alloy:

Fe
$$\underline{203}$$
 + 3C \rightarrow 2Fe + 3C0
8Fe + P $\underline{4}$ \rightarrow 4Fe $\underline{2}$ P

The ferrophosphorus typically contains 59 percent iron and 22 percent phosphorus and is marketed for the production of phosphorus alloys. The vanadium content of ferrophosphorus adds to its value. Should the marketplace be favorable for ferrophosphorus, iron slugs can be added to the furnace charge. Alternately, should a soft market for ferrophosphorus occur, the ferrophosphorus can be converted into high-grade metallurgical iron and fertilizer phosphates. An important degree of freedom is in the ore blending operation, where ores of appropriate iron content may be selected depending on the ferrophosphorus market.

Slag and ferrophosphorus are tapped periodically. The air cooled ferrophosphorus is sold in lumps to the metallurgical industry; no water is involved either in ferrophosphorus cooling or in subsequent product preparation.

The slag may typically contain 38 percent SiO2 and 48 percent CaO, and also contain considerable quantities (depending of course on the ore composition) of Al2O3, CaF2, K2O, and MgO, with traces of uranium and other heavy metals. The slag may be aircooled, but water quenching is more typical. High-density slag is produced by adding water to molten slag in a pit, and by subsequently breaking it up and shipping aggregate for railroad bed or roadbed construction. Alternately, a high-velocity water stream may be used on the molten slag to produce a low density

expanded or granulated slag which has a market in concrete formulation. In either event, some of the fluorides from the slag are captured by the quenching water, either as soluble fluorides or as suspended solids.

There are numerous sources of fumes from the furnace operation. The feeding operation is a source of dust, and fumes are emitted from the electrode penetrations and from tapping. These fumes, consisting of dust, phosphorus vapor (which is immediately oxidized to phosphorus pentoxide), and carbon monoxide are often collected and scrubbed.

The hot furnace gases, consisting of 90 percent CO and 10 percent P4, pass through an electrostatic precipitator to remove the dust before phosphorus condensation. Unless this dust was removed, it would later be emulsified by liquid phosphorus and water, forming large amounts of "phosphorus mud" or sludge which would be difficult and costly to handle.

The precipitator is a most unusual piece of equipment. In the phosphorus process, the precipitator is in the main process stream, as opposed to its usual application in an exhaust stream. Because of this, it is gas-tight (especially since any air would cause phosphorus combustion). It operates at very high temperatures with the inlet gas approaching 540°C (1000°F), and its surfaces must be maintained hot to prevent phosphorus condensation (the dew point of phosphorus is 180°C (356°F)). The precipitator is typically a tube bundle, with the gas passing through the tubes and with a high-voltage wire along the axis of each tube. Both the wire and the tube are mechanically shaken to release the dust into a hopper. In some installations, the dust slurried in water and pumped to a settling pond, and the solids are recycled to the raw feed for recovery of phosphate values (the clarified pond effluent is reused in the slurrying operation).

The high-voltage wires may be insulated from the shell with an oil seal. Contaminated oil is periodically replaced with fresh oil. Alternatively, a quartz seal may be used. The entire unit is heated either electrically or by an inert gas jacket of by-product carbon monoxide combustion gases.

Downstream of the precipitator, the phosphorus is condensed by direct impingement of a hot water spray, which is sometimes augmented by heat-transfer through water-cooled condenser walls. The liquid phosphorus (freezing point 44°C (lll°F)) drains into a water sump, where the water maintains a seal from the atmosphere. This water is partially neutralized by addition of ammonia or caustic to minimize corrosion, and then is recirculated from the sump to the phosphorus condenser.

Liquid phosphorus is stored in steam-heated tanks under a water blanket and is transferred into tank cars by pumping or by hot water displacement. The tank cars also have a protective blanket of water and are equipped with steam coils for remelting at the destination.

Despite very high precipitator removal efficiencies, enough dust reaches the condensers to form some phosphorus mud, which is typically 10 percent dust, 30 percent water, and 60 percent phosphorus.

The condenser exhaust gases are mainly carbon monoxide, which is either burned in a flare or used for heating elsewhere in the plant.

THE PHOSPHORUS-CONSUMING SEGMENT

Phosphoric Acid (Dry Process)

Phosphoric acid is made from elemental phosphorus in the "dry" process, as opposed to the acidulation of phosphate rock in the "wet" process. The wet process is discussed in a separate report dealing with the fertilizer industry. Furnace acid, as dry-process phosphoric acid is called, is relatively pure compared to wet-process acid, as Table 5 indicates. Consequently, the furnace acid is primarily used for preparing foodstuffs, detergents, and other high-grade products, while wet acid is primarily used for preparing fertilizers and animal feed supplements.

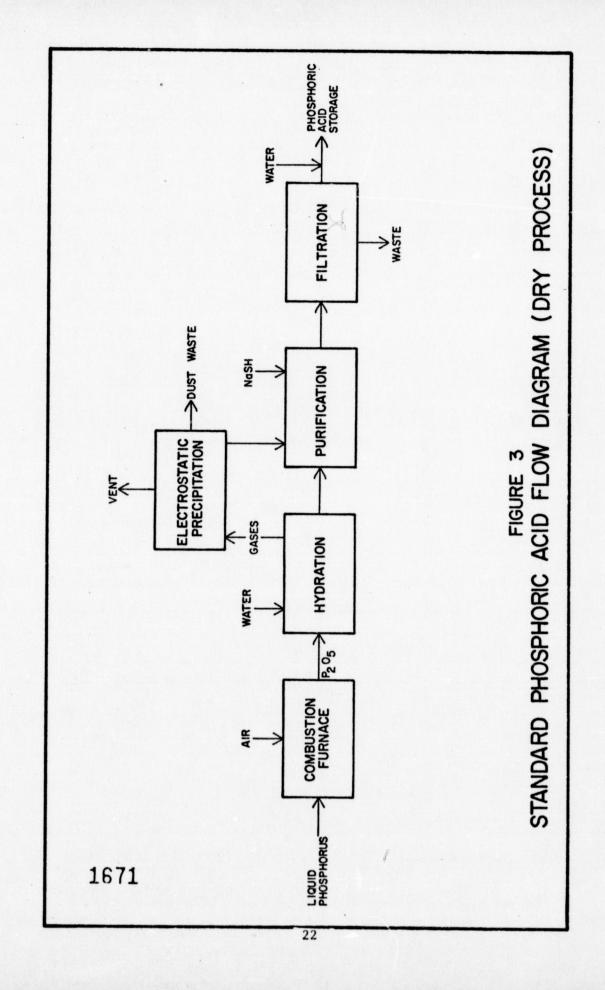
TABLE 5. Impurities in Phosphoric Acid (54% P205)

| | Wet Process Acid | Furnace Acid |
|---------------------------------------------------------------------------------|---------------------------------------|-----------------------------------|
| F, wt % SO3, wt % Al2O3, wt % Fe2O3, wt % Water insolubles, wt % | 0.6 - 1.0 2.7 0.9 1.2 0.8 | 0.007 0.003 0.001 0.0007 |
| Total Impurities, wt % | 6.2 - 6.6 | 0.012 |
| Density, kg/1 (lb/gal) 0 27°C (80°F) Viscosity, cp 0 27°C (80°F) Color | 1.72 (14.3) 85 Black | 1.57 (13.1) 18 Colorless |

In the standard dry process illustrated in Figure 3, liquid phosphorus is burned in air, the resulting gaseous phosphorus pentoxide is absorbed and hydrated in a spray of water, and the mist is collected with an electrostatic precipitator.

The standard reaction may be written:

 $P4 + 502 \rightarrow 2P205 + 6H20 \rightarrow 4H3P04$



Liquid phosphorus is stored under water in tanks heated with steam coils (the freezing point of phosphorus is 44°C (lll°F)). The phosphorus may be fed to the burner by hot-water displacement in a feed tank, or in a loop with a steam-heated displacement water tank and water pump. Alternately, the liquid phosphorus may be pumped directly.

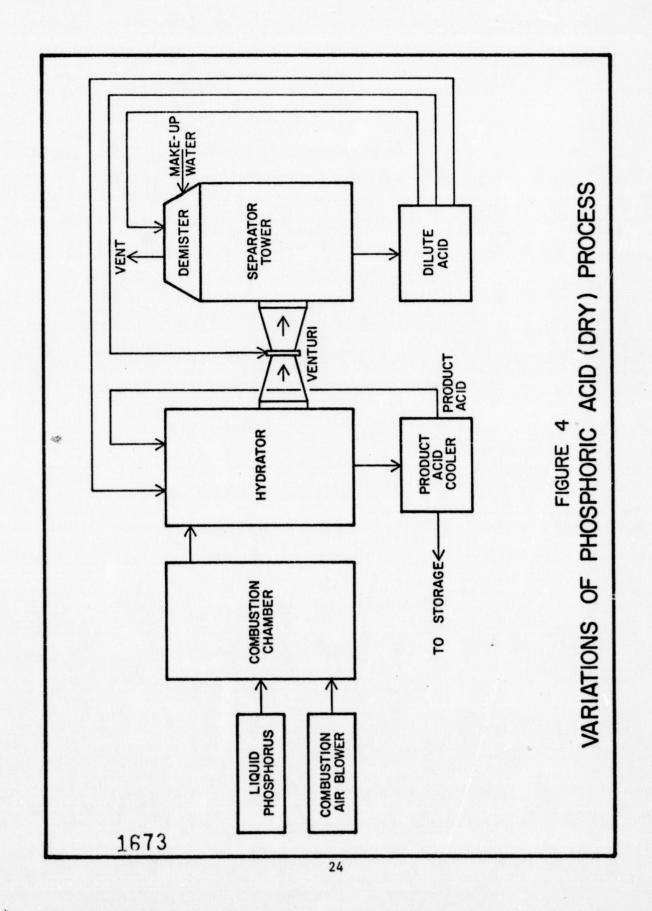
There are variations in the design of the liquid phosphorus injector. Some producers achieve fine atomization using air in a dual-fluid injector (where the injection orifice can be large enough to prevent plugging). To prevent freezing of the phosphorus in upstream portions of the injector and yet to keep the injector tip cool, intricate use of both steam and cooling water has been simultaneously applied. Other designs have proved successful for phosphorus atomization, including the exploitation of extreme turbulence in a pre-combustion zone. Some form of temperature control is required, since red phosphorus formed at combustion temperatures much higher than 1650°C (3000°F) would color the resulting acid and would plug injector orifices.

In the combustion chamber, corrosion by P205 vapors and by hot phosphoric acid (formed from the moisture in the air) is countered by using a graphite lining. The steel shell of the combustion chamber is cooled by running water down its exterior surfaces. This mode of heat transfer is standard; pressurized cooling water is avoided since any leaks would result in premature hydration. Recent plants have been constructed with stainless steel combustion chambers.

The gas exiting from the combustion chamber is typically 540°C (1000°F), and is then hydrated with direct water sprays which also reduce the temperature to 120°C (250°F) or less.

A variation of the standard process, illustrated in Figure 4, uses dilute acid for hydration instead of water. In this case, the make-up water is added in the vapor-liquid separation step. The rationale is that P2O5 vapor is absorbed more easily as the concentration of absorbing acid is increased. Another deviation from the standard process, also shown in Figure 4, is the use of a high-pressure-drop venturi scrubber to complete the somewhat difficult hydration, and a screen-type demister and separation tower instead of an electrostatic precipitator to free the tail gases of the persistent acid mist.

When an electrostatic precipitator is used for collection of the phosphoric acid mist, the corrosivity requires the use of carbon tubes and stainless steel high-voltage wires. Those plants using a high-pressure-drop venturi scrubber and a screen-type demister with a separation tower are of stainless steel construction. Where dilute phosphoric acid is used in the hydrator, the make-up water is added in the separation tower. Regardless of process variation, phosphoric acid is made with consumption of water; no aqueous waste streams are generated by the process.



The product acid is pure, but for the manufacture of food grade acid, traces of arsenic must be removed. Arsenic occurs naturally with phosphorus in the ore (they are both Group V-A elements) at a level of about 0.075 kg of arsenic per kkg of phosphorus (0.15 lb/ton). The arsenic is quantitatively carried through into the acid and is commonly removed by treatment with a soluble sulfide followed by filtration of the insoluble arsenic sulfide.

Phosphorus Pentoxide

The manufacture of solid anhydrous phosphorus pentoxide is similar to the first stages of phosphoric acid manufacture. Liquid phosphorus is burned in an excess of air:

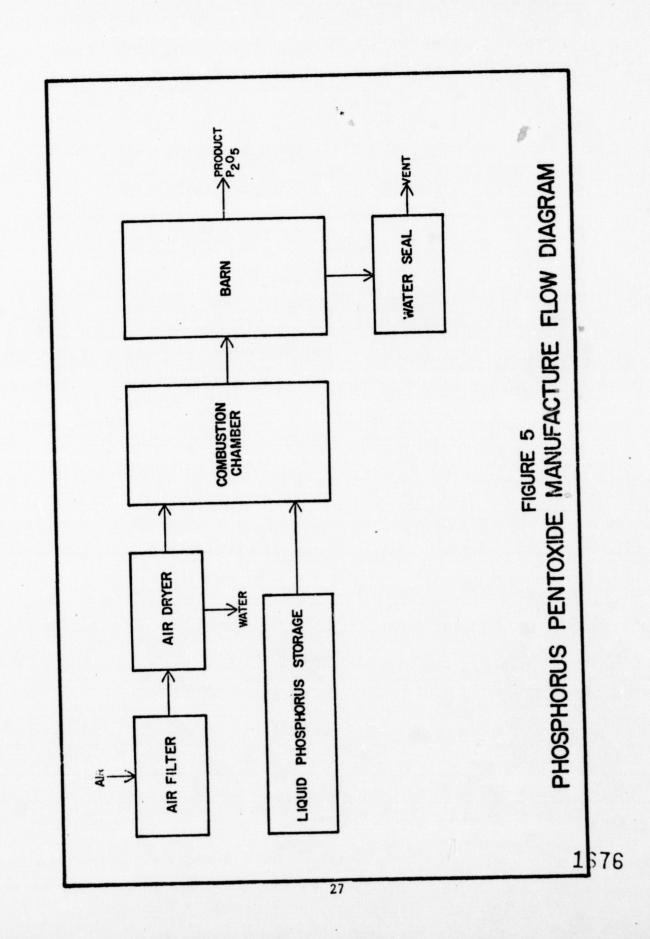
$$P_4(1) + 502 \rightarrow 2P_205(s)$$

Figure 5 is a flow diagram for a standard phosphorus pentoxide manufacturing facility. A significant difference between the two processes is that in the anhydrous phosphorus pentoxide process the air is dried to an extremely low dew point, since any moisture results in a lumpy and agglomerated product not suited for its uses as a reactive drying agent and as a reactive condensing agent in organic synthesis. Typically, the ambient air is filtered, then refrigerated to achieve a dew point of -18 to -7°C (0 to 20°F), and then dried to a dew point of -46°C (-50°F) with silica gel.

After reaction of liquid phosphorus with excess dried air in the combustion chamber, the P2O5 vapor is condensed to a solid in a "barn," which is a room-like structure. Some installations use a more conventional tower for condensation. Both the combustion chamber and the barn (or tower) are cooled by an external flow of water down the surfaces; pressurized cooling water is avoided since any leaks would result in lumpy, unacceptable product.

Condensed phosphorus pentoxide solid is mechanically scraped from the walls using moving chains, and is discharged from the bottom of the barn or tower with a screw conveyor. The gases are vented to the atmosphere through a tail gas water seal which absorbs any P2O5 vapor or solid carry-over. There is usually continuous water addition and overflow for the tail gas seal.

The product particle size is sensitive to the rate of cooling and condensation in the barn or tower. In a barn, the external surface-to-volume ratio is small, a relatively high temperature is maintained in the condensing unit, and rather large crystals may grow. In a tower, heat transfer is more rapid, and the product is very finely divided. One installation uses two towers in series; the first has much higher heat transfer rates and results in a coarser product than the second, and the products from the two towers are separately packaged.



Phosphorus Pentasulfide

The standard process for the manufacture of phosphorus pentasulfide, shown in Figure 6, is by direct union of the elements, both in liquid form:

$$P_{\underline{4}}(1) + 10s(1) \longrightarrow 2P_{\underline{2}}s_{\underline{5}}(1)$$

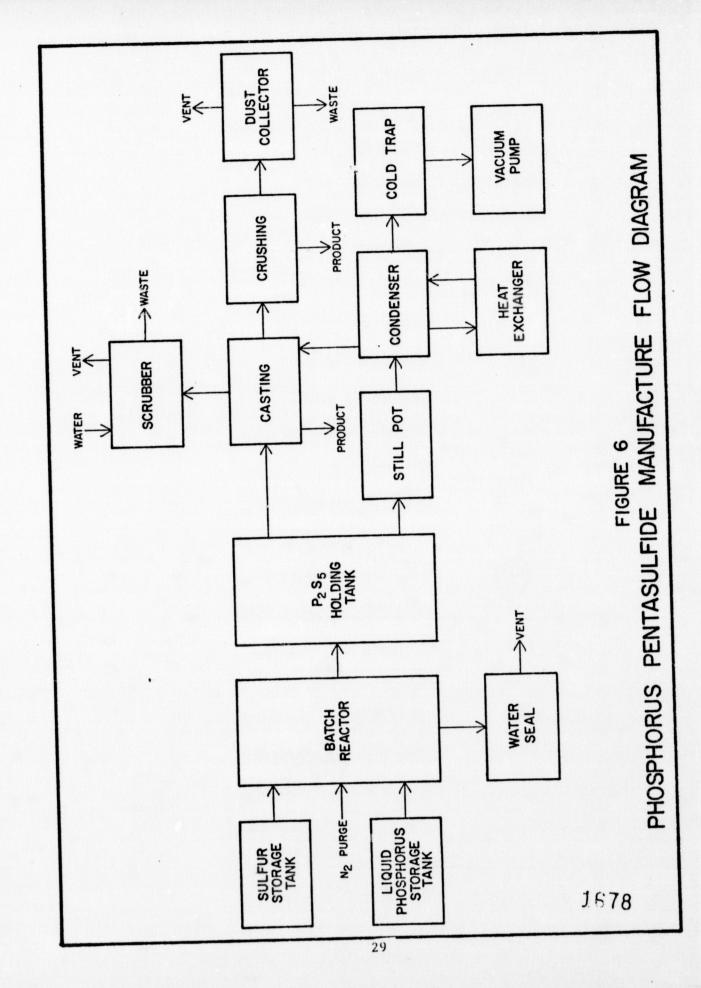
The largest use of phosphorus pentasulfide is for the manufacture of lubricating oil additives.

Liquid sulfur (melting point 113°C (230°F)) is transferred from a steam-heated storage tank using submerged pumps, and liquid phosphorus (melting point 44°C (111°F)) is transferred by hot water displacement. The highly exothermic reaction is usually carried out as a batch operation in stirred cast iron pots. A "heel" of molten P2S5 (melting point 282°C (540°F)) from the previous batch is used to absorb the initial heat of reaction. Liquid phosphorus and liquid sulfur are incrementally added. Since the reactants and the product are extremely flammable at the reaction temperature, the reactor is continuously purged with nitrogen. A water seal is used in the vent line.

The batches from multiple reactors are forced into an electrically heated (300°C (570°F)) P2S5 holding tank by nitrogen pressure. Some of the P2S5 is converted directly into product, while the rest is purified. Liquid P2S5 from the holding tank that is to be sold is cast directly into drums or into cones. When the molten product contacts air during casting, it ignites, and fumes of P2O5 and SO2 are generated. A fume hood and water scrubber are used. The cones, after cooling, are crushed and packaged; solid P2S5 does not auto-ignite in air. The dust from the crushing operation is removed in a dry separation system such as a cyclone.

The liquid P2S5 that is to be purified may be vacuum distilled (normal boiling point is 515°C (960°F)) in a continuous system. The condenser is cooled by a high-temperature heat transfer fluid, which in turn is cooled in a water-cooled heat exchanger. The condenser is operated between the melting and boiling points of the product. Molten purified P2S5 is then cast and crushed, sharing the fume scrubber and dust collection systems with the impure product operation.

An alternate mode of purification is the washing of crushed P2S5 with carbon disulfide, in which the by-products phosphorus sesquisulfide (P4S3) and free sulfur are soluble.



Phocoborus Production

Phosphorus Trichloride

Phosphorus trichloride, used extensively in organic synthesis, is manufactured directly from the elements:

$$P_{\underline{4}}(1) + 6C1\underline{2}(g) \rightarrow 4PC1\underline{3}(1)$$

The standard process is shown in Figure 7. Liquid phosphorus is charged to a jacketed batch reactor. Chlorine is bubbled through the charge, and phosphorus trichloride product (melting point -112°C (-173°F)), boiling point 74°C (165°F), is refluxed until all the phosphorus is consumed. Some cooling water is used in the reactor jacket since the formation of PCl3 is exothermic. Care is taken to avoid an excess of chlorine; otherwise, phosphorus pentachloride is formed.

When the reaction is complete, the cooling water to the reflux condenser is turned off, steam is supplied to the reactor jacket, and the product of the batch distillation is condensed and collected.

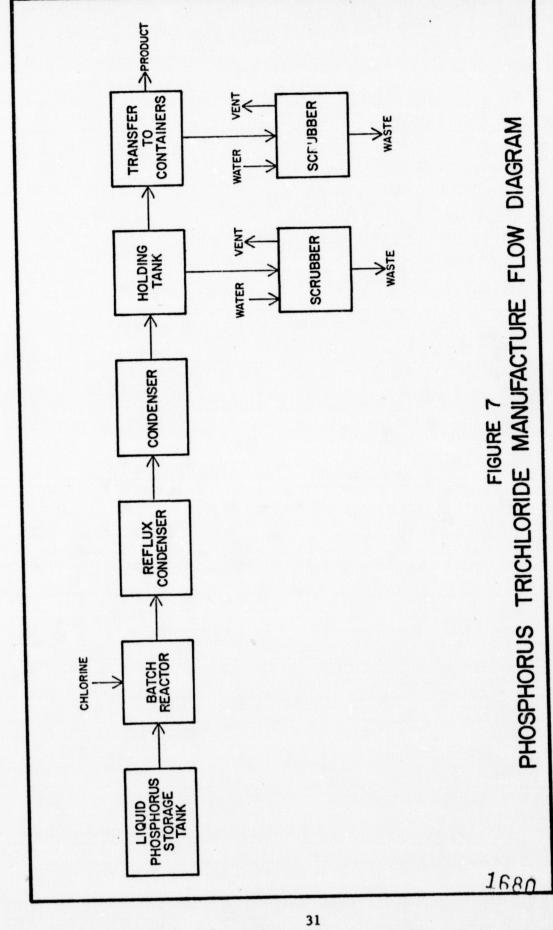
A water scrubber collects hydrochloric acid and phosphorous acid, the hydrolysis products of PCl3 vapors:

The vapor pressure of the product is sufficiently high so that the fumes from transferring the product into shipping containers are also collected and scrubbed.

In a variation of the standard process, the reaction is conducted semi-continuously instead of batch-wise. The reflux condenser of Figure 7 is tailored so that only a small fraction of the PCl3 is withdrawn as product; the larger fraction of condensed PCl3 returns to the reactor and serves as the working fluid and heat sink for the reaction, since elemental phosphorus is somewhat soluble in PCl3. Gaseous chlorine is added continuously, and liquid phosphorus is added incrementally.

No provision is generally made for continuous or frequent withdrawal of residue from the reactor either in the batch process or in the semi-continuous process. Instead, the residue is permitted to accumulate, and the reactor is shut down for cleanout infrequently.

Phosphorus trichloride is corrosive and is often shipped in returnable nickel drums. Before use, these drums are thoroughly washed with water and steam cleaned. Some recent use has been made of non-returnable epoxy-lined steel drums.



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Phosphorus Oxychloride

Phosphorus oxychloride, used in the preparation of organic phosphate esters and pharmaceuticals, is manufactured by the reaction of liquid phosphorus trichloride, chlorine, and solid phosphorus pentoxide:

$3 \text{ PCl}_{3}(1) + 3 \text{ Cl}_{2}(g) + P205(s) \rightarrow 5 \text{ POCl}_{3}(1)$

The standard process, illustrated in Figure 8, is carried out in a batch reactor and still which are very similar to the standard phosphorus trichloride equipment. Liquid phosphorus trichloride is charged to the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture while the PCl3 (boiling point 74°C (165°F)) and later the POCl3 (boiling point 105°C (221°F)) are refluxed. When the reaction is complete, steam is supplied to the reactor jacket, the water to the reflux condenser is shut off, and the product is distilled over and collected.

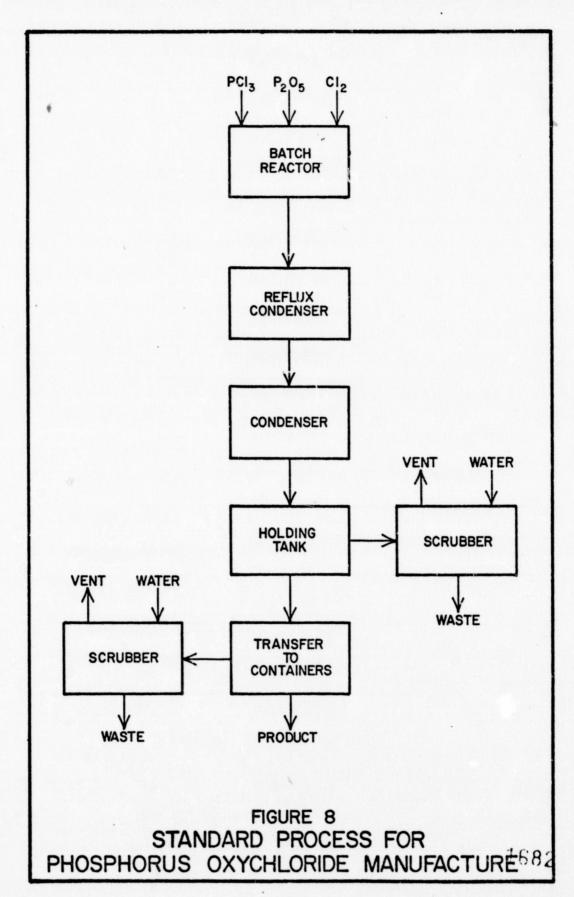
An alternative process for the manufacture of phosphorus oxychloride from phosphorus trichloride is also in commercial use. As is shown in Figure 9, dried air is used as the oxidant in a batch process. A water-cooled reflux condenser is used as in the standard process, except that a refrigerated condenser is added in series to ensure total reflux of the PCl3 upstream of a water scrubber for the tail gas. The significant difference is that in the air-oxidation process a large quantity of non-condensible gas (nitrogen and excess oxygen) is involved.

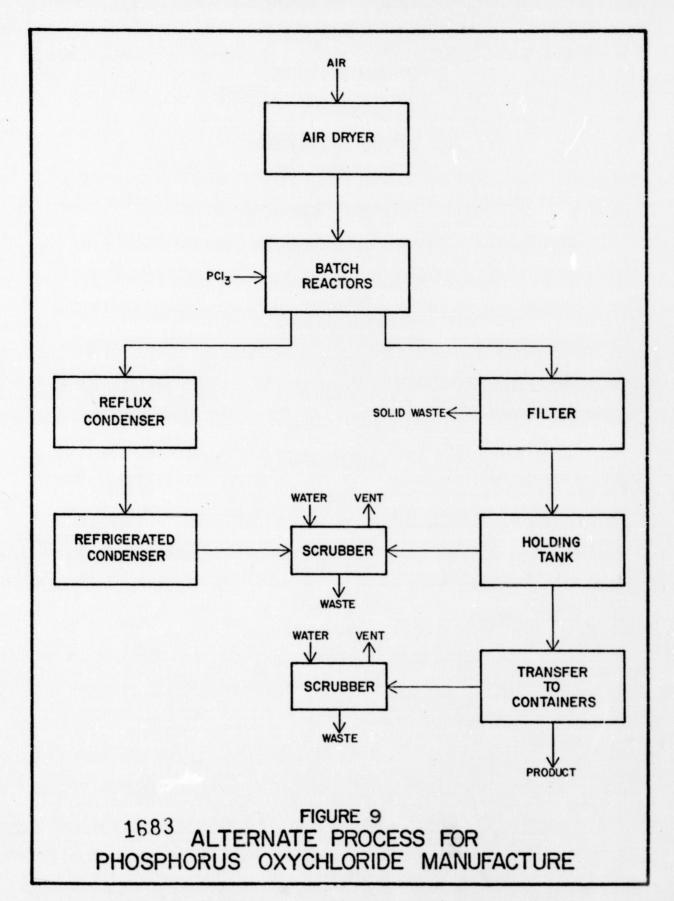
Instead of a final distillation step, the product POCl3 is filtered, with periodic changing of the cartridge filter elements.

Water scrubbers collect hydrochloric acid and phosphoric acid, the hydrolysis products of POCl3 vapors, both from the reaction/distillation equipment and from transferring operations (for either process):

POC13 + 3H2O→3HC1 + H3PO4

Like phosphorus trichloride, phosphorus oxychloride is extremely corrosive and is shipped in returnable nickel drums. Before reuse, these drums are thoroughly washed with water and steam cleaned. Some recent use has been made of non-returnable epoxy lined steel drums.





THE PHOSPHATE SEGMENT

Sodium Tripolyphosphate

Sodium tripolyphosphate is manufactured by the neutralization in mix tanks of phosphoric acid by soda ash or by caustic soda and soda ash, with the subsequent calcining of the dried mono- and di-sodium phosphate crystals. Figure 10 is a flow diagram of the standard process. The sodium tripolyphosphate product is widely used in detergents and in water-softening applications. In the neutralization step, the amount of raw material is measured and controlled to yield monosodium orthophosphate and disodium orthophosphate in a 1:2 mole ratio:

6H3PO4 + 5Na2CO3 -> 2NaH2PO4 + 4Na2HPO4 + 5H2O + 5CO2, or 9H3PO4 + 5NaOH + 5Na2CO3 -> 3NaH2PO4 + 6Na2HPO4 + 10H2O + 5CO2

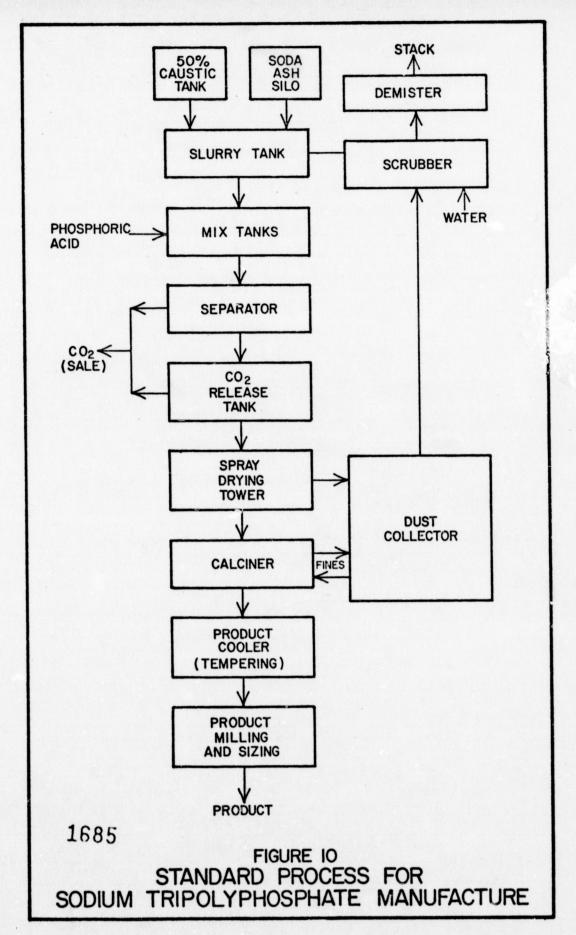
In either process variation, the final pH in the mix tank is very carefully adjusted by small additions of either phosphoric acid or caustic soda solution.

The mixture of sodium orthophosphates is spray dried or drum dried and the solids calcined to produce the sodium tripolyphosphate:

 $NaH_{2}PO_{4} + 2 Na_{2}HPO_{4} \rightarrow Na_{5}P_{3}O_{10} + 2 H_{2}O$

The product is then slowly cooled or tempered to preserve the condensed form of the phosphates. If the product is chilled too rapidly, it will revert to a mixture of the meta- and polyphosphates:

 $Na5P3010 \rightarrow Na3P03 + Na2P207$



Calcium Phosphates

The non-fertilizer calcium phosphates are made by the neutralization of phosphoric acid with lime. Although the reactions are chemically similar, the processes for manufacturing the different calcium phosphates differ substantially from one another in the amount and type of lime used and the amount of process water used (See Figures 11 and 12).

Relatively pure, food grade monocalcium phosphate (MCP) is made in a stirred batch reactor from furnace acid and lime slurry:

$2H\underline{3}PO\underline{4} + Ca(OH)\underline{2} \rightarrow Ca(H\underline{2}PO\underline{4})2 \cdot H\underline{2}O + H\underline{2}O$

An excess of phosphoric acid maintained during the batch addition cycle inhibits the formation of dicalcium phosphate. A minimum quantity of process water is used. The heat of the reaction liberates some water as steam in the reactor, and the remaining water is evaporated in a vacuum dryer, a steam heated drum dryer, or a spray dryer. The anhydrous MCP is produced by using CaO (quicklime) and in carrying out the reaction at 140°C (310°F) so that water is driven off as it is produced.

Relatively pure food grade tricalcium phosphate (TCP) is made in a similar manner to MCP, except that an excess of lime slurry maintained during the batch addition cycle inhibits formation of dicalcium phosphate:

$2H\underline{3}PO\underline{4} + 3Ca(OH)\underline{2} \rightarrow Ca\underline{3}(PO\underline{4})\underline{2} + 6H\underline{2}O$

Like MCP, the TCP is dried to prevent excessive product temperatures.

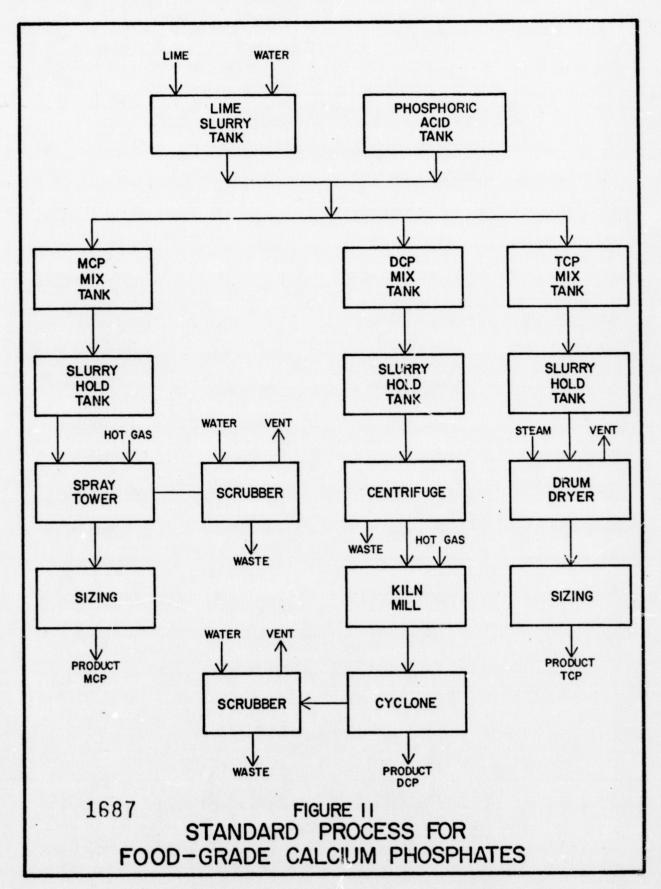
Relatively pure, food grade dicalcium phosphate (DCP) is made in batch stirred reactors, but with much more process water than for either MCP or TCP:

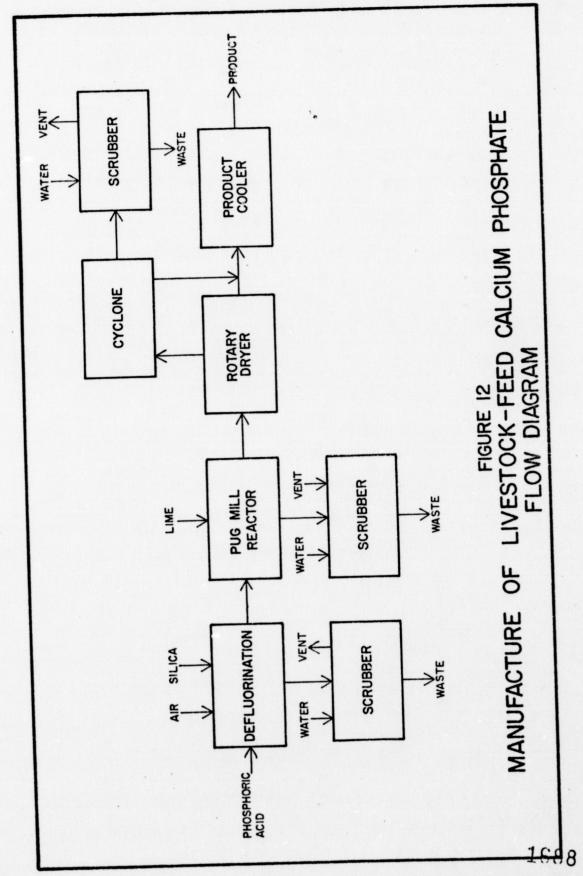
$H3PO4 + Ca(OH) 2 \rightarrow CaHPO4 . 2H2O$

The stoichiometry for DCP manufacture is critical; any excess H3PO4 during the batch addition cycle would result in some MCP and any excess Ca(OH) 2 would result in some TCP. The excess water in the DCP reactor is to ensure homogeneity so that the local stoichiometry is as balanced as the overall reactor stoichiometry.

As a result of the excess of water used, the reaction mixture is a pumpable slurry as opposed to the pasty consistency of MCP and TCP. This DCP is mechanically dewatered before drying.

product (5-000 lb/ton) wi





(5 lb/ton). If all of this dust became part of the sludge, the

Dicalcium phosphate (DCP) is also manufactured for livestock feed supplement use, with much lower specifications on product purity. Hence, the reaction can be conducted without excess water, since some MCP and/or TCP in the DCP product is perfectly tolerable. The pasty reaction product is normally dried in a rotary dryer. Powdered limestone, CaCO3, may be used instead of lime. If quicklime is used, the drying step may be bypassed.

Another significant process difference is that non-food grade wet process phosphoric acid is normally used for this product. The DCP plants defluorinate the acid unless this step was accomplished by the acid producer. Wet process phosphoric acid contains approximately 1 percent fluoride in various forms. The defluorination consists of treating the heated acid with finely-divided silica and steaming or aerating, which liberates silicon tetrafluoride gas:

Wet scrubbers then hydrolyze and collect this gas as fluosilicic acid and silicic acid:

$$3 \operatorname{sif}_{4} + 3\operatorname{H}_{2}0 \longrightarrow 2\operatorname{H}_{2}\operatorname{sif}_{6} + \operatorname{H}_{2}\operatorname{sio}_{3}$$

The hot defluorinated phosphoric acid is then charged to the reactor to make dicalcium phosphate.

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

In developing effluent limitations guidelines and standards of performance for new sources for a given industry, a judgment must be made by the Environmental Protection Agency as to whether effluent limitations and standards are appropriate for different segments (subcategories) within the industry. The factors considered in determining whether such subcategories are justified for the phosphate category of point sources are:

wastes generated
treatability of waste waters
manufacturing process
raw materials
plant size and age
product
land availability
air pollution control equipment

WASTES GENERATED

Tables 7, 8, and 9 in section V show the raw waste loads for the phosphate category. Suspended solids and dissolved phosphates are common raw waste water constituents for phosphorus, food grade calcium phosphates, and feed grade calcium phosphates. Dissolved solids are present in concentrations significantly above background for all the chemicals studied. Elemental phosphorus can be a waste water constituent common to all of the phosphorus can be a waste water constituent common to all of the phosphate manufacturing industry if the phossy transport water is not returned to the phosphorus producing plant. Sulfates, fluorides and alkalinity are constituents and parameters specific to phosphorus production. Furthermore, the amount of waste water (425,000 l/kkg of P4) resulting from the production of phosphorus is several orders of magnitude greater than that generated from any of the other processes. The chemicals H3PO4, P2O5, P2S5, PCl3, and POCl3 commonly generate acidic wastes and phosphates.

TREATABILITY OF WASTE WATERS

Phosphorus production clearly stands alone on the basis of waste water treatability. The large amount of waste water produced (425,000 l/kkg P4) presents special problems. It is commonly practiced within the industry to return phossy transport water to the phosphorus plant. Therefore, the problem of treating elemental phosphorus is only a phosphorus plant problem or can be so handled that it will be a problem unique to phosphorus plants.

The chemicals H3PO4, P2O5, P2S5, PCl3, and POCl3 present similar treatability problems in that acidic wastes are encountered. PCl3 and POCl3 present more difficult problems because the resultant chloride ions are difficult to remove.

The calcium phosphates involve similar treatment problems (suspended solids and phosphates). Defluorination of animal feed grade calcium phosphates will produce fluoride wastes, but the proposed treatment schemes will handle this waste constituent.

MANUFACTURING PROCESS

Manufacturing process is the principal factor used to determine subcategories. Phosphorus production is an ore reduction process involving large electric furnaces and large amounts of raw material and slag. Ferrophosphorus is a by-product in the phosphorus reaction and is always considered along with phosphorus when considering effluent quality.

The chemicals H3PO4, P2O5, PCl3, and POCl3 are all similar in that a gaseous intermediate or product is encountered somewhere in the reaction sequence. The synthesis of P2S5 resembles the above in that water and air must be completely absent in the whole or parts of the reaction sequence.

Sodium tripolyphosphate and the calcium phosphates are produced by the neutralization of phosphoric acid by alkaline slurries.

RAW MATERIALS

The following raw materials are used for each process:

| <u>Materials</u> |
|------------------|
| |

| P4 & Fe2P H3PO4 | Phosphate Ore | Coke(C) SiO <u>2</u> |
|-------------------------------------------------|---------------|-------------------------|
| H <u>3</u> PO <u>4</u> P <u>2</u> 0 <u>5</u> | P <u>4</u> | 0 <u>2</u> |
| P2S5 | P <u>4</u> | S |
| PC13 | P <u>4</u> | C12 |
| POC13 | PC1 <u>3</u> | $C1\overline{2} (P205)$ |
| Na <u>5</u> P <u>3</u> 0 <u>10</u> | H3PO4 | Na2CO3 (NaOH) |
| Calcium Phosphates | H3PO4 | Ca (OH) 2 |

When the nonphosphorus compounds are excluded, four subcategories become evident on the basis of raw material. The POCl3 process is so like the PCl3 process, however, that it is included in the latter subcategory.

PLANT SIZE AND AGE

. . 2 .

Plant size will not affect the quantities of wastes produced (kg per kkg of product) to such a degree that subcategorization would be warranted. The same basic production processes for each chemical are used throughout the phosphate industry. Plant age will not affect the quantities of wastes produced to the degree where subcategorization is warranted. Another point is that there are no really new plants, and consequently the situation does not exist where new technologies make older technologies obsolete. With respect to economics it is particularly difficult

phosphoric acid may amount to an average of 1 kg/kkg (2 1D/ton),

to assess the effects of waste water treatment. The chemicals covered by this report serve as raw materials or intermediates for other products produced by the same company. The theoretical profitability of a single plant may well not decide if operations are to continue at that site. With this in mind it would be difficult if not impossible to establish criteria based on the economics of plant size or age for the purpose of subcategorization.

PRODUCT

The product does have some bearing on the waste water quality when the product or vapors from the product or intermediate come into contact with water. This topic has already been indirectly discussed under wastes generated. In summary, phosphorus production is associated with elemental phosphorus, phosphorus, fluoride, suspended and dissolved solids. The production of H3PO4, P2O5, P2S5, PCl3 and POCl3 result in phosphates, dissolved solids, and acids in the waste waters. The production of Na2P3O1C and the calcium phosphates result in phosphates, suspended and dissolved solids in the effluent.

LAND AVAILABILITY

Removal of suspended solids from raw waste waters is most easily accomplished by use of large settling ponds. This will be the principle concern for land availability. The plants in this category are located, however, in rural sites where the problem of land availability is minimized.

AIR POLLUTION CONTROL EQUIPMENT

All of the chemicals covered in this study use wet scrubbers or water systems in the process itself which amount to scrubbers. Therefore this is not a topic for subcategorization. Furthermore, it is recommended that dry air pollution control equipment either precede or replace wet scrubbers in order to reduce scrubber water contamination. Volatilization of hazardous substances such as fluorine from neutralization and settling ponds is insignificant.

SUBCATEGORIES

The factors that entered into the selection of subcategories are: wastes generated, treatability of waste waters, product, and particularly raw material and manufacturing process. Three subcategories were considered necessary for purposes of establishing effluent limitations guidelines:

- Phosphorus Production a.
 - phosphorus 1.
 - 2. ferrophosphorus
- Phosphorus Consuming b.
 - phosphoric acid (dry process) 1.
 - 2.
 - phosphorus pentoxide phosphorus pentasulfide phosphorus trichloride 3.
 - 4.
 - phosphorus oxychloride 5.
- Phosphate c.
 - sodium tripolyphosphate 1.
 - 2. Calcium phosphates
 - i. animal feed grade
 - ii. food grade

Transfer and Storage of Phosphorus, 1.0 kg/kkg (2 15)

SECTION V

WATER USE AND WASTE CHARACTERIZATION

INTRODUCTION

With the background of manufacturing technology discussed in Section III, this section discusses the specific water uses in the phosphate mufacturing industry and the raw wastes from this industry before control and/or treatment of these wastes. and Section V are intended to be generally Section III descriptive of the industry; i.e., they outline the standard manufacturing processes and the standard raw waste loads that are common to the great bulk of plants in the industry. It is not until Section VII, Control and Treatment Technology, and Section IX, Best Practicable Control Technology Currently Available, that distinctions are made (and quantitatively supported by independently verified sampling data of plant effluents) within the industry, pointing out those notable plants which have already achieved significant reduction or total elimination of polluting discharges.

The following discussion therefore, should not be taken as implying that the raw waste loads quoted are always actual plant discharges. Rather, they are intended to describe the total waste management problem originally faced by any plant in the industry. In actuality, significant abatement steps have been taken by some plants within the industry. By fully explaining the total waste management problem (in terms of raw waste loads), the control and treatment steps can be later explained and evaluated.

SPECIFIC WATER USES

Water is primarily used in the phosphate manufacturing industry for eight principal purposes:

Non-contact Cooling Water
Process and Product Water
Transport Water
Contact Cooling or Heating Water
Atmospheric Seal Water
Scrubber Water
Auxiliary Process Water
Miscellaneous Uses

Non-Contact Cooling Water

This type of water is used without contacting the reactants, such as in a tube-in-shell heat exchanger. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases. Probably the single most important process waste control technique, particularly for subsequent

treatment feasibility and economics, is segregation of noncontact cooling water from process water.

Non-contact cooling water is generally of two types in the industry. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is oncethrough cooling water whose source is generally a river, lake, or tidal estuary, and the water is returned to the same source from which it was taken.

The only waste effluent from the recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, and alkali metals such as sodium and potassium produced by ion exchange units. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending on the type of unit employed in the plant.

Process and Product Water

The process or product water generally is that which comes in contact with the product and stays with the product as an integral part, such as the quenching, hydrolysis and dilution water used in phosphoric acid manufacture, or the water used as a reaction medium in food grade dicalcium phosphate manufacture.

Transport Water

Water may be used for transporting reactants or products between unit operations. An example is the use of water for transferring (by displacement) liquid phosphorus. Another example is the transfer of electrostatic precipitator dust in phosphorus manufacture as a slurry in water.

Since intimate contact between the process materials and transport water occurs, this water may generally contain dissolved or suspended materials and so is classified as process water.

Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes in direct contact with process waters. A prime example is the large quantity of water used to quench the slag from phosphorus furnaces; another is the water used to condense the gaseous phosphorus after it is produced in the furnaces.

Other direct contact cooling or heating water use such as that for contact steam heating and/or drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than 1695

the barometric condenser water and is easier to treat for waste effluents.

Atmospheric Seal Water

Because some of the materials in this industry spontaneously ignite on contact with the oxygen in air, the air is kept out of reaction vessels with a water seal. Liquid phosphorus is universally protected by storing under a water blanket. These seal waters are considered as process waters.

Scrubber Water

Throughout this industry, water scrubbers are used to remove process vapors and/or dusts from tail gases and from gaseous process streams. The used scrubber water is regarded as process water since direct and intimate contact has occurred. The resultant solution or suspension may contain impurities or may be too dilute a solution to reuse or recover and thus is discharged.

Auxiliary Process Water

This water is used in medium quantities by the typical plant for auxiliary operations such as ion exchange regeneration, make-up water to boilers with a resultant boiler blowdown, equipment washing, storage and shipping tank washing, and spill and leak washdown. The volume of waste water from these operations is generally low in quantity but highly concentrated.

Miscellaneous Water Sources

These water sources vary widely among the plants originating from floor washing and cleanup, safety showers, eye wash stations, sanitary uses and storm run-off. The resultant streams are either non-contaminated or slightly contaminated with wastes. The general practice is to discharge such streams without treatment except for sanitary waste.

PROCESS WASTE CHARACTERIZATION

The descriptions of the manufacturing processes in Section III, and the flow diagrams included in that Section, qualitatively discussed the sources of wastes. The following discussion is intended to describe these waste streams both in quantity and in composition. These waste streams are the "raw" wastes before control or treatment (which is separately discussed in Section VII).

Aqueous wastes emanating from air pollution abatement equipment are considered as process wastes in this study.

The following sections quantify the raw process wastes in each segment of the industry. A discussion of the source, nature, and amount of these wastes for each segment is followed by a table summarizing the standard raw waste load.

Various plants in the industry differ significantly in the degree of process and cooling water recirculation. Hence, the waste water quantities and constituent concentrations quoted may be grossly different from plant-to-plant. However, the raw loads in kg per kkg of product (lb/ton) are dependent primarily on the manufacturing processes and are therefore much more representative of the entire industry.

The Phosphorus Production Subcategory

The discussion of phosphorus manufacturing technology in Section III and the flow diagram of Figure 2 qualitatively pointed out the following streams emanating from the process (in addition, of course, to the phosphorus product stream):

By-products: Slag, Ferrophosphorus, and Carbon Monoxide
Non-contact Cooling Water
Electrostatic Precipitator Dust
Calciner Precipitator Dust
Calciner and Furnace Fume Scrubber Liquor
Phosphorus Condenser Liquor (Aqueous phase)
Phosphorus Sludge (or mud)
Slag Quench Liquor

The following sections discuss each of the above in quantitative detail, and identify which are typically returned to the process and which are classified as raw waste streams from the manufacturing operation.

By-product Streams

The by-products of the phosphorus manufacturing operation are:

| | kq/kkq | 1b/ton |
|------------------------|--------|--------|
| Ferrophosphorus | 300 | 600 |
| Slag (CaSiO <u>3</u>) | 8,900 | 17,800 |
| CO gas | 2,800 | 5,600 |

Both ferrophosphorus and slag are sold, and the carbon mc oxide is either used to generate heat in the process or is otherwise burned on site. Hence, none of the above three materials is considered a waste.

The quench water used for the by-product slag is separately di cussed as a waste stream.

The by-product ferrophosphorus is cast as it is tapped from the furnace and air-cooled. The solids are then broken up and shipped. No water is used specifically for ferrophosphorus, and there are no wastes accountable for ferrophosphorus manufacture.

Non-Contact Cooling Water

Phosphorus production facilities generate huge quantities of heat. The electrical power consumption is approximately 15,500 kwh/kkg (48 million Btu/ton). An additional 8,100 kwh/kkg (25 million Btu/ton) are generated by combustion of the by-product carbon monoxide. Some of this energy, 6,100 kwh/kkg (19 million Btu/ton), is absorbed in the endothermic furnace reaction, and some is absorbed by the endothermic calcining operation. Other portions of this energy are released to the atmosphere by burning of waste carbon monoxide (that not used for calcining) and by convection, radiation and evaporative losses from the equipment and process materials. Still other portions are absorbed by waters in the calcining process and furnace from scrubbers, in the phosphorus condenser, and in the slag quenching operation.

After accounting for the above energy demands, a significant quantity of heat is absorbed by non-contact cooling water for the furnace shell, the crucible bottom, the fume hood, the tap holes, the electrode fixtures, the electrical transformer, and for any indirect phosphorus condensation. The quantity of this water is highly variable from plant to plant, and depends on the furnace design, the furnace size, and the degree of recirculation (through heat exchangers with other water streams or through cooling towers), whether or not cooling water is used in series different requirements, the inlet temperature of the available cooling water, and the ambient air temperature. Plant 181 uses 325,000 1/kkg of product (78,000 gal/ton); Plant 159 uses 38,000 1/kkg (9,000 gal/ton); and TVA at Muscle Shoals, Alabama. (5) uses 130,000 1/kkg (31,000 gal/ton).

Electrostatic Precipitator Dust

The high-temperature electrostatic precipitator removes dusts from the furnace gases before these gases are condensed for recovery of phosphorus. These dusts may contain up to 50 percent P205, and therefore find value either as a fertilizer for sale or for return to the process. In the latter case, they are transported to the ore blending head end of the plant. One TVA scheme slurries the dust for transport; the slurry is pumped to a settling pond, the settled solids are fed to the ore - blending unit, and the pond overflow is reused in the slurrying operation.

The quantity of precipitator dust is approximately 125 kg/kkg of product (250 lb/ton). Regardless of the method of sale or reuse, the precipitator dust is not a waste material to be disposed of from the plant.

Calciner Precipitator Dust

Dry dust collectors are used in the calcining operation, upstream of wet scrubbing systems. The dry fine dusts collected are recycled directly to the sizing and calcining operations. The collected and recycled fines may amount to as much as 30 percent of the net production from the nodulizing process.

There is no plant discharge of dry calciner precipitator dusts; therefore this is not a component of the plant's raw waste load.

Calciner and Furnace Fume Scrubber Liquor

Water scrubbers are used for air pollution abatement for the calciner exhaust stream (downstream of dry dust collection), for furnace fumes, for ore sizing dusts, for coke handling dusts, for raw material feeding operation dusts, and for furnace taphole (slag and ferrophosphorus) fumes. The scrubber liquor contains suspended solids (which are mainly SiO2 and Fe2O3), phosphates and sulfates as dissolved solids, and a large quantity of fluorides. To explain the presence of these fluorides in the scrubber liquor, Table 6 lists the quantities of materials phosphate rock presented as pounds per ton of commercial phosphorus ultimately produced after normalizing of 26 percent P205 content. From Table 6, the average quantity of F in ore is 275 kg/kkg of P4 (550 lb/ton). Approximately 8 percent of this quantity of F, or 22 kg/kkg (44 lb/ton), is volatilized in the ore calcining operation, and is subsequently a constituent of the scrubber liquor.

This scrubber liquor is highly acidic for three reasons: the sulfur (as SO3) forms sulfuric acid; the P2O5 forms phosphoric acid; and the fluorine, which is released in the form of silicon tetrafluoride, forms fluosilicic acid and silicic acid on hydrolysis.

The quantity of scrubber liquor wasted depends on the degree of recirculation of this liquor from a sump back to the scrubbers. TVA at Muscle Shoals circulates approximately 21,000 1/kkg of

Moreover, since purity requirements are considerably less severe

TABLE 6

Composition of Commercial Phosphate Rocks (12)

Expressed as kg per kkg (lb/ton) of Phosphorus Produced

| Constituent | Florida Pebb Furnace kg/kkg | le | Tenne Brown <u>Furnace</u> kg/kkg <u>l</u> | Rock | Phosphor Low G | ic Acid |
|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| P205 Ca0 Mg0 A1203 Fe203 Si02 S03 F CO2 Organic Carbon Na20 K20 | 2,600 3,800 35 125 155 725 215 305 330 40 10 | 5,200 7,600 70 250 310 1,450 430 610 660 80 20 | 2,600 3,550 75 1,230 760 3,150 50 270 150 35 35 | 5,200 7,100 150 2,460 1,520 6,300 100 540 300 70 70 | 2,600 3,150 190 810 550 3,750 260 245 550 685 205 135 | 5,200 6,300 380 1,620 1,100 7,500 520 490 1,100 1,370 410 270 |

product (5,000 lb/ton) with a portion bled off to control the composition. This scrubber liquor is of the following composition:

| Constituent | | Concentration, % |
|--------------|---|------------------|
| F | | 3.1 |
| SiO <u>2</u> | | 1.1 |
| P205 | | * 0.2 |
| Fe203 | ü | 0.1 |
| S | | 1.7 |

If the fluoride concentration of 3.1 percent is equated to a standard raw waste load (as previously discussed) of 22 kg/kkg (44 lb/ton), the quantities of other scrubber liquor components may be calculated:

| Constituent | Raw Was | ste Load |
|------------------------|---------|----------|
| | kq/kkq | 1b/ton |
| F. | 22 | 44 |
| Si0 <u>2</u> | 8 | 16 |
| P205 | 1.5 | 3 |
| Fe <u>2</u> 0 <u>3</u> | 0.5 | 1 |
| S | 12 | 24 |

The total CaCO3 acidity of the scrubber liquor, calculated from the above constituent quantities, is 60 kg/kkg (120 lb/ton).

Other plants do not recirculate scrubber liquor; the volume wasted is much greater and the constituent concentrations are much smaller, but the raw waste loads (in kg/kkg of product) should be comparable. Plant 181 does not directly recirculate the liquor, and uses 300,000 l/kkg (71,000 gal/ton) for scrubbing.

Phosphorus Condenser Liquor

The furnace gases pass from the electrostatic dust precipitator to the phosphorus condenser, where a recirculating water spray condenses the product. The condenser liquor is maintained at approximately 60°C (140°F), high enough to prevent solidification of the phosphorus (freezing point 44°C (112°F)). This condenser liquor is "phossy water", essentially a colloidal dispersion of phosphorus in water, since the solubility at 20°C (68°F) is only 3.0 mg/l. Depending on how intimate the water/phosphorus contact was, the phosphorus content of phossy water may be as high as several weight percent.

The condenser liquor also contains constituents other than elemental phosphorus: fluoride, phosphate, and silica. Using the average F content of ore (from Table 6) of 275 kg/kkg, plus the estimate that 12 percent of the F in the ore volatilizes in the

furnace and is therefore equivalent to 33 kg/kkg (66 lb/ton), and by accounting for 6 kg of F per kkg (12 lb/ton/ ton) which is collected in the precipitator dust and in the phosphorus sludge ash, a raw waste load of F is derived of 27 kg/kkg (54 lb/ton) in the condenser liquor. This condenser liquor is not acidic despite the hydrolysis of P205 and SiF4 to H3P04, H2SiF6, and H2SiO3 because aqueous ammonia or caustic is added to prevent

undue corrosion in the condenser.

There are other sources of phossy water within the plant. Storage tanks for phosphorus have a water blanket, which is discharged on phosphorus transfer. Railroad cars are cleaned by washing with water. Phosphorus may be purified by washing with water. Together, all sources of phossy water wastes amount to about 5,400 1/kkg (1,300 gal/ton), and at a concentration of 1,700 mg/l, the quantity of phosphorus wastes amounts to about 9 kg/kkg produced (18 lb/ton), as reported by TVA.

At TVA, the condenser liquor is recirculated at the rate of 33,000 1/kkg (8,000 gal/ton). Other plants may differ significantly in the quantity of phossy water circulated, but the raw wastes (in kg/kkg of product) should be fairly uniform. For example, Plant 181, which does not directly recirculate its condenser water, uses 84,000 1/kkg (20,000 gal/ton), with an additional 17,000 1/kkg (4,000 gal/ton) for phosphorus handling and storage.

To calculate the raw waste loads of phosphate and silica in the condenser liquor, the following TVA recirculated-liquor composition was used:

| Constituent | Concentration, % |
|--------------------------|------------------|
| F | 8.3 |
| P205 | 5.0 |
| $\overline{\text{sio}2}$ | 4.2 |

Equating 8.3 percent F with the previously-derived 27 kg/kkg of F, the raw waste loads of P205 and Si02 become respectively 16.5 kg/kkg (33 lb/ton) and 13.5 kg/kkg (27 lb/ton).

Phosphorus Sludge

In addition to phossy water, the phosphorus condenser sump also collects phosphorus sludge, which is a colloidal suspension typically 10 percent dust, 30 percent water and 60 percent phosphorus. The quantity of sludge formed is directly dependent on the quantity of dust that escapes electrostatic precipitation, hence the very large investment made for highly efficient precipitators.

Using 125 kg of dust (per kkg of product) collected by the electrostatic precipitator, and assuming a 98 percent collection efficiency, the dust reaching the condenser amounts to 2.5 kg/kkg

(5 lb/ton). If all of this dust became part of the sludge, the sludge quantity would be 25 kg/kkg (50 lb/ton) of product, and it would contain 15 kg/kkg (30 lb/ton) of elemental phosphorus.

This sludge is then universally processed for recovery of phosphorus, typically by centrifugation. A 96 percent recovery has been reported, with the product (subsequently returned to the process) averaging 92 to 96 percent phosphorus. The remaining 4 percent of the phosphorus in the sludge is burned in a phosphoric acid unit, so that no wastes emanate from the plant.

Other methods for processing the sludge which also result in no plant effluent include heating in a slowly rotating drum in an inert atmosphere to drive off phosphorus vapor, which is then condensed with a water spray into a sump. The solid residue obtained is completely free of elemental phosphorus and can be safely landfilled or recycled to the feed preparation section of the plant.

Slag Quenching Liquor

Slags from phosphorus furnaces are mainly SiO2 and CaO, and would also contain Al2O3, K2O, Na2O, and MgO in amounts consistent with the initial ore composition. In addition to these oxides, phosphate rock may contain 0.1-0.2 kg/kkg (0.2-0.4 lb/ton) of uranium in the ore, and the radiation levels of both the slag and the quench waters must be appropriately noted. Other constituents of the slag presenting problems for quench water pollution control are fluoride and phosphate. Approximately 80 percent of the original F in the phosphate rock, 220 kg/kkg of P4 (440 lb/ton), referring to Table 6, winds up in the slag. About 2.7 percent of the original P2O5 in the phosphate rock, 70 kg/kkg (140 lbs/ton), winds up in the slag.

At Plant 181, approximately 24,600 l/kkg (5,900 gal/ton) may be used for quenching the slag, with the slag quench liquor having the following composition and raw waste loads:

| Constituent | Concentration, mg/l | Raw Waste Load | | |
|------------------------|---------------------|----------------|-----------|--|
| | | kq/kkq P4 | 1b/ton P4 | |
| Total Suspended Solids | 800 | 20 | 40 | |
| Total Dissolved Solids | 1,700 | 42 | 85 | |
| Phosphates (as P) | 12 | 0.3 | 0.6 | |
| Sulfate (as S) | 1,000 | 25 | 50 | |
| Fe | 14 | 0.35 | 0.7 | |
| F | 170 | 4.5 | 9 | |
| Total Alkalinity | 230 | 5.5 | 11 | |

TABLE 7

Summary of Raw Wastes from Phosphorus Manufacture

Note: Waste water quantities and constituent concentrations are highly variable, depending on degree of recirculation, but the raw waste loads should be representative.

| | Calciner Scrubber <u>Liquor</u> | Phosphorus Condenser Plus Other Phossy Water | Slag Quenching <u>Water</u> | Composite Waste |
|-------------------------------------------------------------------------|---------------------------------------|-------------------------------------------------------|--------------------------------------------|----------------------------------------|
| Waste Water Quantity, 1/kkg gal/ton | 300,000 | 100,000 24,000 | 25,000 6,000 | 425,000 102,000 |
| Raw Waste Load, kg/kkg TSS P4 PO4 SO4 F Total Acidity Total Alkalinity | 8.5 - 2 36 22 60 | 13.5 9 22 - 27 - | 20.5 - 1 75 4.5 - 5.5 | 42.5 9 25 111 53.5 54.5 |
| Raw Waste Load, 1b/ton TSS P4 PO4 SO4 F Total Acidity Total Alkalinity | 17 - 4 72 44 120 | 18 44 - 54 | 41 - 2 150 9 - | 85 18 50 222 107 109 |
| Concentrations, mg/1 TSS P4 PO4 SO4 F Total Acidity Total Alkalinity | 1 28 - 7 120 73 200 | 90 220 3 - 3 270 | 820 - 40 3,000 180 - 220 | 100 21 59 260 126 128 |

The Phosphorus Consuming Subcategory

No direct process aqueous wastes are generated in this segment of the industry. The raw wastes arise from phosphorus storage and transfer, from wet scrubbing of tail gases, from vessel cleaning, and from leaks and spills.

Phossy Water Wastes

Because phosphorus is transported and stored under a water blanket, phossy water is a raw waste material at phosphorus using plants as well as at phosphorus producing plants. The standard procedure when liquid phosphorus is transferred from a rail car to the using plant's storage tank is to pump the displaced phossy water from the storage tank back into the emptying rail car as practiced at Plants 037 and 192. Instead of being wasted at the phosphorus-using plant, the phossy water is shipped back to the phosphorus-producing facility for treatment and/or re-use. Therefore, standard raw phossy water wastes at the phosphorus using plants are due to surges or to anomalies in the storage tank water level control system rather than to the direct wasting of all displaced water.

A more insidious source of phossy water may arise at phosphorus consuming plants. Should reactor contents containing phosphorus ever be dumped into a sewer as a result of operator error, emergency conditions, or inadvertent leaks or spills, the phosphorus would remain at the low points in the sewer line generally as a solid (melting point 44°C (lll°F)) and would contact all water flowing in that sewer from that time on. Since phosphorus burns when exposed to air (autoignition temperature 93°C), there is general reluctance to clean it out. The common practice is to ensure a continuous water, flow to prevent fire.

The typical phosphorus loss for phosphorus consuming plants is 1 kg lost to phossy water per kkg consumed (2 lb/ton). Whenever phosphorus is tranferred by displacement, 580 liters of water are displaced per kkg of phosphorus (140 gal/ton). These values are equivalent to a phosphorus concentration of 1700 mg/l. For comparison, a typical phosphorus content in phossy water at a phosphorus producing plant has also been reported at 1700 mg/l.

Phosphoric Acid Manufacture

The production of phosphoric acid by the "dry" process from elemental phosphorus consumes a total of about 380 liters of water per kkg of product (92 gal/ton) for both the hydration and the acid dilution steps. The cooling water requirements are typically 92,000 liters per kkg of product (22,000 gal/ton); but with recycle of cooling water, the make-up cooling water requirement is approximately 4,600 liters per kkg of product (1,100 gal/ton). There is no aqueous process waste from notable phosphoric acid Plants 003, 006, 042, and 075. Despite good housekeeping at a notable plant, however, leaks or spills of 1/05

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phosphoric acid may amount to an average of 1 kg/kkg (2 lb/ton), with a range of 0 to 2.5 kg/kkg (0 to 5 lb/ton).

Where food grade phosphoric acid is produced, a standard raw waste of 0.1 kg/kkg (0.2 lb/ton) of arsenic sulfide is precipitated by addition of a soluble sulfide (H2S, Na2S, NaHS) and filtered out of the acid. An additional 0.75 kg/kkg (1.5 lb/ton) of filter-aid material may accompany the sulfide as a solid waste.

Phosphorus Pentoxide Manufacture

The waste water from the tail seals on the condensing towers typically contains 0.25 kg/kkg (0.5 lb/ton) of H3PO4 (100 percent basis). Approximately 500 l/kkg (120 gal/ton) of water may be used, resulting in a concentration of 470 mg/l for the effluent bleed.

The inlet air dryer silica gel is regenerated often, but is renewed very infrequently (perhaps every ten years). The wasted material is typically landfilled.

Approximately 29,000 1/kkg (7,000 gal/ton) of non-contact cooling water are used.

Phosphorus Pentasulfide Manufacture

The water seals on the batch reactor vent lines accumulate a mixture of phosphorus mud and lower phosphorus sulfides. These seals are cleaned once a week, and the residue amounts to 0.15 kg/kkg (0.3 lb/ton). This residue is hazardous and flammable and is typically buried.

Should any batch be aborted (a rare occurrence) because of agitator failure, cast iron pot failure, or other reason, the material is disposed of by incineration.

The dust collected by a cyclone from the P2S5 crushing operation amounts to 1 kg/kkg (2 lb/ton).

The still pot for the vacuum distillation step accumulates impurities, which include carbon and iron sulfur compounds and glassy phosphates. Most important, the residues contain arsenic pentasulfide, which is higher-boiling than the corresponding phosphorus pentasulfide. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton) of arsenic which is equivalent to 0.05 kg of As2S5 per kkg of product P2S5 (0.1 lb/ton). The entire still pot residue is about 0.5 kg/kkg (1 lb/ton). Periodically, these residues are removed and the solids are broken up and buried. Approximately 17,000 l/kkg (4,000 gal/ton) of non-contact cooling water is used.

In the casting of liquid P2S5, the fumes from burning liquid (molten P2S5 auto-ignited) are scrubbed. Typically, the scrubber water contains 1.25 kg of combined P2O5 and SO2 per kkg of product P2S5 (2.5 lb/ton). Because both P2O5 and SO2 are absorbed by a water scrubber only with difficulty, the water flow rate is high, 30,000 l/kkg (7,200 gal/ton). These values reduce the concentrations of PO2-3 and SO3-2 in the scrubber effluent of 17 and 34 mg/l, respectively. Much lower scrubber flow rates could be used should weak caustic or lime be used instead of water.

Phosphorus Trichloride Manufacture

The batch or semicontinuous reactor/stills accumulate residues which are periodically but infrequently removed. These residues contain arsenic trichloride, which is higher-boiling than the corresponding phosphorus trichloride. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton) of arsenic, which is equivalent to 0.05 kg of AsCl3 per kkg of product PCl3 (0.1 lb/ton). This is about half the quantity of total residue in the stills (exclusive of residual PCl3 from the last batch or run before shutdown).

The average non-contact cooling water requirement is 54,000 l/kkg (13,000 gal/ton).

Water scrubbers collect PCl3 vapors from the reaction, the product distillation, the product storage, and the product transfer operations and hydrolyze these vapors to HCl and to H3PO3 (which may subsequently be oxidized to H3PO4). The quantity of PCl3 collected is highly dependent on the efficiency of the upstream condensers, since PCl3 is highly volatile:

| Temp, °C | Temp, or | PC13 Vapor Pressure, mm Hq(27) |
|----------|----------|--------------------------------|
| 20 | 68 | 99 |
| 40 | 104 | 235 |
| 60 | 140 | 690 ' |
| 76 | 169 | 760 |

At Plant 037, sufficient heat transfer area was provided in the condensers to limit the raw waste load to 3 kg of HCl plus 2.5 kg of H3PO3 per kkg of product PCl3 (6 lb/ton and 5 lb/ton). Approximately 5,000 l/kkg (1,200 gal/ton) of scrubber water were used to collect these wastes. Other smaller waste quantities of HCl and H3PO3 generated from tank car and returnable container cleaning operations have been included in these quantities.

These quantities are based on the most reliable data available at Plant 037, overall material balances of product PCl3 shipped vs. elemental phosphorus received. These data, validated over long periods of time for profitability purposes, show a total loss of phosphorus trichloride of 5 kg/kkg (10 lb/ton). An estimated breakdown of this loss is:

ingreases the bacterial multiplication rate when the

Transfer and Storage of Phosphorus,
Reactor/Still Residues,
Scrubber for Distillation Tail Gases,
Transfer of PCl3,

1.0 kg/kkg (2 lb/ton)
2.5 kg/kkg (5 lb/ton)
1.0 kg/kkg (2 lb/ton)

Other than the estimated loss of elemental phosphorus and the reactor/still residues, the losses which become water-borne raw wastes amount to 3.5 kg/kkg (7 lb/ton). Upon hydrolysis, this stoichiometrically becomes 3 kg/kkg (6 lb/ton) of HCl plus 2.5 kg/kkg (5 lb/ton) of H3PO3. These material-balance data have their long-term confirmation. been used because of measurements of waste water flow rates and of waste water constituent analysis were not relied on in this case since accurate flow rate measurements were not possible in the existing plant configuration and since no statistically meaningful analytical data had been collected. The acid wastes from washing tank cars and tank trucks and from washing used POCl3 filter elements are very small at present. Water use data taken from Plant 037, supplemented by an independent analysis of the waste water, yielded the results in Table 8. Total raw waste generated in truck-loading, in tank-car cleaning, and in filter-element washing is 0.014 kg/kkg (0.028 lb/ton) of HCl plus 0.003 kg/kkg (0.007 lb/ton) of total phosphates.

Phosphorus Oxychloride Manufacture

The water scrubber for the distillation operation in the standard process (using P205 and C12) typically collects 1.5 kg of HCl (anhydrous basis) and 0.25 kg of H3P04 (100 percent basis) per kkg of product POC13 (3 lb/ton and 0.5 lb/ton), and the scrubber for POC13 transferring collects about 0.2 kg of HCl and 0.15 kg of H3P04 per kkg of product (0.4 lb/ton and 0.3 lb/ton). Allowing for small wastes from returnable container cleaning operations, the standard raw waste load is 2 kg of HCl and 0.5 kg of H3P04 per kkg of product (4 lb/ton and 1 lb/ton). Approximately 2,500 l/kkg (600 gal/ton) of water are used, so that the raw waste concentrations are 800 mg/l HCl and 200 mg/l H3P04.

The source of the above data on raw waste loads was Plant 147 records and plant personnel analysis of these records. An independent verification of these results was not judged valid since at this plant neither an accurate determination of waste water flow rate nor the collection of a distinct waste water sample from each unit operation contributing to the waste load was practical, and since statistically valid background data were not at hand.

These waste quantities for POCl3 manufacture are somewhat smaller than for PCl3 manufacture since POCl3 is less volatile (boiling point 107°C). In the batch process, the refluxing liquid is all PCl3 at the start, but becomes increasingly richer in POCl3.

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of the estuary that can be adversely affected by extreme

TABLE 8

Minor Wastes from Plant 037 (PC13 and POC13)

| | | Truck-Loading Vent Scrubber | Tank Car Cleanout Water | Filter Element Washout Drum |
|---------------|-----------------|-----------------------------------|-------------------------------|-----------------------------------|
| | | | | |
| Water Use: | 1/kkg | 8.8 | 10.5 | 0.46 |
| | gal/ton | 2.1 | 2.5 | 0.11 |
| Constituent A | nalysis, mg/ | 1: | | |
| Ch | loride | 340 | 715 | 6,480 |
| То | tal PO <u>4</u> | 260 | 26 | 590 |
| To | tal Acidity | 660 | - | 18,200 |
| Raw Waste Loa | d, kg/kkg: | | | |
| Ch | loride | 0.0030 | 0.0075 | 0.0030 |
| То | tal PO4 | 0.0023 | 0.0003 | 0.0003 |
| То | tal Acidity | 0.0058 | | 0.0083 |
| Raw Waste Loa | d, lb/ton: | | | |
| Ch | loride | 0.006 | 0.015 | 0.006 |
| To | tal PO4 | 0.005 | 0.001 | 0.001 |
| To | tal Acidity | 0.012 | | 0.017 |

The air-oxidation process presents a much more difficult task for the reflux condenser, since the vapors are highly diluted with non-condensibles. With the use of refrigerated condensers, however, the measured raw waste load is no different for this process. At Plant 037, data collected over three months from the reactor/still scrubber for POCl3 manufacture, which had an estimated flow rate of 1,800 l/kkg (430 gal/ton), had average net values of:

Chloride 669 mg/l CaCO3 acidity 1,213 mg/l

These data reduce to a raw waste of 1.2 kg/kkg (2.4 lb/ton) of HCl plus 0.35 kg/kkg (0.7 lb/ton) of H3PO4, which are extremely close to the corresponding values for Plant 147.

Where product POCl3 is filtered, the used filter elements are first washed to hydrolyze the residual POCl3. Disposable elements are then landfilled. The quantity of filtered solids retained on the elements is only a very small fraction of the weight of the used element. The elements are washed in a 55-gallon drum, so that a very small quantity of waste water (and of acid wastes) is involved compared to the scrubber waste load. Although there is no continuous withdrawal of residues from POCl3 distillations, very little residue accumulates. Twice a year this residue (mostly glassy phosphates) is washed out with hot water.

The non-contact cooling water requirement for POCl3 manufacture by either the standard or the alternate method is approximately 50,000 1/kkg (12,000 gal/ton).

Variability of Raw Wastes from the Production of Phosphorus Trioxide and Phosphorus Oxychloride

The data below indicate the variability of concentrations in the raw waste load at Plant 037.

| Pate (1973) | Cacoa Acidity, mg/l | Chloride. mg/l |
|--------------------------------|---------------------|----------------|
| 2/27 | 1170 | 560 |
| 2/28 | 1220 | 603 |
| 3/1 | 1720 | 922 |
| 4/19 | 850 | 447 |
| 4/23 | 480 | 305 |
| 4/24 | 950 | 532 |
| 4/25 | 1430 | 851 |
| 4/26 | 1250 | 589 |
| | 1300 | 1035 |
| 4/27 | 1120 | 518 |
| 4/30 | 1470 | 1040 |
| 5/1 | 1690 | 716 |
| 5/2 | | 773 |
| 5/3 | 280 | 603 |
| 5/4 | 1340 | 1000 |
| 5/7 | 1810 | |
| 5/8 | 1220 | 574 |
| 5/9 | 1296 | 716 |
| | 1217 | 687 |
| Mean | 384 | 208 |
| Std. Deviation | 384 | 208 |
| 95% Conf. Int. (Single Day) | +_614 | +_441 |

In this case, there was no damping capacity; the acidity and chloride concentrations were closely coupled to the manufacturing process. The comparison of the 95% confidence intervals with the daily data show only one point of 17 (for acidity) and no points outside (for chloride).

Based on these very limited samples of data, it appears that the classical statistics may be applied, but with extreme caution.

For the above sets of data from Plant 037, a value of $(X + 3\sigma) / X$ might represent a maximum allowable daily reading as a multiple of the mean:

Parameter

 $(x + 3\sigma) / x$

Acidity Concentration Chloride Concentration 1.95

This maximum allowable value would be extremely liberal, since a Students "t" value of 3 is equivalent to less than one reading in 100 being unduly rejected. To be even more liberal (since the data base for this analysis is extremely skimpy), the maximum value from the above table will be assumed, so that the effluent limitation guideline for the manufacture of PCl3 and POCl3 should be a maximum daily value no greater than twice the mean (as represented by consecutive 30-day averages).

pH can be controlled much more closely than other parameters. Hence, it is recommended that the pH limitation be met at all times.

TABLE 9
Summary of Raw Waste from Phosphorus-Concuming Plants

| | H ₃ PO ₄ (75%) | P2 ⁰ 5 | ^p 2 ^S 5 | PC13 | P0C1 ₃ |
|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------------------------|
| Phossy Water: P4 conc, ppm 1/kkg P4 consumed kgP4/kkg P4 consumed gal/ton P4 consumed 1b /ton P4 consumed | 1,700 580 1 140 2 | 1,700 580 1 140 2 | 1,700 580 1 140 2 | 1,700 580 1 140 2 | ======================================= |
| Process Water Wasted: 1/kkg Pdt gal/ton Pdt | | 500 120 | 30,000 7,200 | 5,000 1,200 | 2,500 |
| Raw Wuste Load, kg/kkg Pdt: HC1 H ₂ S03 H ₃ P0 ₃ + H ₃ P0 ₄ | 1 | 0.25 | 1 0.5 | 3 2.5 | 2 0.5 |
| Raw Waste Load, 1b /ton Pdt: HC1 H2S03 H3P03 + H3P04 | 2 | 0.5 | 2 | 6 5 | -4 1, |
| Concentrations, mg/1: HC1 H ₂ SO ₃ H ₃ PO ₃ + H ₃ PO ₄ | High | 470 | 34 17 | 600 500 | 800 200 |
| Process Water Consumed: 1/kkg Pdt. gal/ton Pdt | 380 92 | | | | |
| Cooling Mater Used: 1/kkg Pdt gal/ton Pdt | 91,000 22,000 | 29,000 | 16,600 | 54,000 13,000 | 50,000 12,000 |
| Solid Wastes, kg/kkg Pdt: As Compounds Total Residues | 0.1 | | 0.05 | 0.05 0.05 | <0.05 |
| Solid Wastes, 1b /ton Pdt: As Compounds Total Residues | 0.2 | == | 0.1 | 0.1 | <0.1 |

The Phosphate Subcategory

The aqueous wastes from this segment of the industry arise from the use of wet dust scrubbing equipment for the finely divided solid products, and from processes which use excess process water which may become a waste stream.

Sodium Tripolyphosphate Manufacture

Exemplary Plants 006, 042, and 119 have no process wastes. The dust collected from the spray dryer gaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray dryer vent line upstream of the scrubbing operation.

The neutralization step requires a total of 1,040 1/ kkg (250 gal/ton), of which 290 1/kkg (70 gal/ton) are recycled from the scrubber. Make-up water, 750 1/kkg (180 gal/ton), is added since water is evaporated in the product drying step. The make-up water is softened, and regeneration of the softener combined with boiler and cooling tower blowdowns amounts to 210 1/kkg (50 gal/ton), 70 percent of which is from water treatment regeneration and 30 percent from blowdowns. These blowdown wastes typically contain 1,500 mg/l of dissolved chlorides.

Calcium Phosphates

The raw aqueous wastes from the manufacture of food grade calcium phosphates are from two primary and approximately equal sources: the centrate of filtrate from dewatering of the dicalcium phosphate slurry and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely-divided calcium phosphate solids. It is normal practice in an integrated plant to partially recycle the scrubber water and to partially use the DCP centrate or filtrate as make-up scrubber water, as at Plant 003. The total raw wastes from this system are typically 4,200 1/kkg (1,000 gal/ton) containing 100 kg/kkg (200 lb/ton) of solids (a concentration of 2.4 percent). An additional 30 kg/kkg (60 lb/ton) of dissolved solids (0.7 percent of this waste stream) originates from phosphoric acid mists in the scrubbers and from excess phosphoric acid in the reaction liquid.

For non-food grade dicalcium phosphate plants, the water scrubbers which collect airborne solids normally operate at partial recycle. Since there is no waste from a dewatering operation, and since dry dust collection typically precedes wet scrubbing, the raw wastes are considerably smaller than for the food grade operation. Dry dust collection is typical since only one or two products are made, so that the collected solids may be added directly to the product stream without extensive segregation.

Moreover, since purity requirements are considerably less severe, the product stream can tolerate such additions. With the above measures, the wet scrubber wastes are typically 420 1/kkg (100 gal/ton) containing 22.5 kg/kkg (45 lb/ton) of suspended solids (a concentration of 5 percent) plus 4 kg/kkg (8 lb/ton) of dissolved phosphates from acid mists (0.7 percent). At Plant 182, this bleed stream from the wet scrubber recirculation system is charged directly to the neutralization reactor; hence, this plant had no discharge. As an added feature, this notable plant used cooling water blowdown as make-up to the airborne-solids scrubbing system, thereby eliminating all aqueous discharges (except for the effluent from regeneration of the water softener).

For the non-food grade plants, however, acid defluorination is an additional source of raw wastes (unless already defluorinated acid is delivered to the plant). Wet-process phosphoric acid (54 percent P205) contains approximately 1 percent fluorine. Upon silica treatment, 13.5 kg per kkg of acid (27 lb/ton), or 10.5 kg of silicon tetrafluoride product dicalcium phosphate dihydrate When hydrolyzed in the acid lb/ton), are liberated. (21 scrubber, the raw waste contains 12 kg/kkg product (24 lb/ton) of combined fluosilicic acid (H2SiF6), hydrofluoric acid (HF) and silicic acid (H2SiO3). These raw wastes are contained in a scrubber water flow of 6,300 liters/ kkg (1,500 gal/ton), so that the combined concentration of fluosilicic acid, hydrofluoric acid and silicic acid is 1,900 mg/l. For any plant manufacturing calcium phosphates of any grade, non-contact cooling water is used in reactors and/or in dried product coolers.

Other possible sources of aqueous wastes are regeneration of water softeners and storm water runoff (all exterior surfaces of calcium phosphate plants become coated with fine lime and/or phosphate dusts).

In dry product plants, a significant housecleaning effort must be continually maintained. In non-food grade calcium phosphate plants, the dry product sweepings (from dust, spills, etc.) are added to the process stream. In food grade plants, however, the sweepings (consisting of lime, lime grit, and calcium phosphates) are wasted. Typically, this solid waste amounts to 10 kg/kkg (20 lb/ton).

TABLE 10
Summary of Raw Wastes from Phosphate Plants

| | Sodium Tripoly- | Food Grade <u>Calcium Phosphates</u> Solids | | Animal Feed Calcium Phosphates Acid Deflu- Solids | |
|-----------------------|--------------------|---------------------------------------------|-----------|---------------------------------------------------|-----------|
| | Phosphate | Dewatering | Scrubbing | orination_ | Scrubbing |
| Process Water Wasted: | | | | | |
| 1/kkg Pdt | 0 | 2,100 | 2,100 | 6,300 | 420 |
| gal/ton Pdt | 0 | 500 | 500 | 1,500 | 100 |
| Raw Waste Load, | £10° | | | | |
| kg/kkg Pdt: | | | | | |
| TSS | • | 50 | 50 | - | 22.5 |
| Dissolved PO4 | | 15 | 15 | - | 4 |
| HF, H2SiF6, H2SiO3 | | - | / • | 12 | • |
| Raw Waste Load, | | | | | |
| 1b/ton Pdt: | | | | | |
| TSS | | 100 | 100 | | 45 |
| Dissolved P4 | | 30 | . 30 | - | 8 |
| HF, H2SiF6, H2SiO3 | - | | - | 24 | • |
| Concentrations, mg/1: | | | | | |
| TSS | - | 24,000 | 24,000 | - | 54,000 |
| Dissolved PO4 | | 7,000 | 7,000 | - | 7,000 |
| HF, H2SiF6, H2SiO3 | | • | - | 1,900 | -1 |
| TDS, mq/l | | 7,000 | 7,000 | 1,900 | 7,000 |
| Solid Wastes: | | | | | |
| kg/kkg Pdt | 0 | | LO | - | - 00 |
| lb/ton Pdt | 0 | | 20 | - | - |

SECTION VI

SELECTION OF POLLUTION PARAMETERS

INTRODUCTION

Section V of this report quantitatively discussed the raw wastes generated in the phosphate manufacturing industry. The following were identified as being constituents of the industry's process waste waters:

Suspended Solids
Phosphate and Elemental Phosphorus
Sulfates and Sulfites
Fluoride
Chloride
Dissolved Solids
pH, Acidity and Alkalinity
Temperature
Arsenic
Vanadium, Cadmium, and Radioactivity

The following discussion examines each of the above and their impact on receiving waterways from a chemical a physical and a biological viewpoint. Additional constituents such as hexavalent chromium, iron, alkalinity, and hardness, which are of typical concern whenever blowdowns from cooling towers, boilers and water treatment facilities are involved, are noted here but are not discussed in detail in this study (which deals more specifically with the process wastes of the phosphate industry).

PROPERTIES OF THE POLLUTANTS AND POLLUTANT PARAMETERS

The following paragraphs describe the chemical, physical and biological properties of the pollutants and pollutant parameters that exist for this industry. The undesirable characteristics that these parameters exhibit or indicate are stated, giving reason to why they were selected.

TOTAL SUSPENDED SOLIDS

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning

ground of fish. Deposits containing organic materials may also deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries, paper and pulp, beverages, dairy products, laundries, dyeing, photography, cooling systems and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or cnto clay particles.

Solids may be suspended in water for a time and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are esthetically displeasing. When they settle to form sludge deposits on the stream or lake bed they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. Organic solids of a decomposable nature use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

PHOS PHORUS

During the past 30 years, a formidable case has developed for the belief that increasing standing crops of aquatic plant growths, which often interfere with water uses and are nuisances to man, frequently are caused by increasing supplies of phosphorus. Such phenomena are associated with a condition of accelerated eutrophication or aging of waters. It is generally recognized that phosphorus is not the sole cause of eutrophication, but there is evidence to substantiate that it is frequently the key

element in all of the elements required by fresh water plants and is generally present in the least amount relative to need. Therefore, an increase in phosphorus allows use of other, already present, nutrients for plant growths. Phosphorus is usually described, for this reason, as a "limiting factor."

When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities are immediately apparent. Dense populations of pond weeds make swimming dangerous. Boating and water skiing and sometimes fishing may be eliminated because of the mass of vegetation that serves as a physical impediment to those activities. Plant populations have been associated with stunted fish populations and with poor fishing. Plant nuisances emit vile stenches, impart tastes and odors to water supplies, reduce the efficiency of industrial and municipal water treatment, impair beauty, reduce or restrict resort trade, lower waterfront property values, cause skin rashes to man during water lontact, and serve as a desired substrate and breeding ground for flies.

Phosphorus in the elemental form is particularly toxic, and subject to bioaccumulation in much the same way as mercury. Colloidal elemental phosphorus will poison marine fish (causing skin tissue breakdown and discoloration). Also, phosphorus is capable of being concentrated and will accumulate in organs and soft tissues. Experiments have shown that marine fish will concentrate phosphorus from water containing as little as 1 ug/l.

SULFATES AND SULFITES

Sulfites are oxidized to sulfates in streams, exerting a chemical oxygen demand on the streams.

Sulfates are not particularly harmful, but are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

FLUORIDES

As the most reactive non-metal, fluorine is never found free in nature. It is a constituent of fluorite or fluorspar (calcium fluoride) in sedimentary rocks and of cryolite (sodium aluminum fluoride) in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

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Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children.

Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

CHLORIDE

Dissolved chlorides are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

Sodium and calcium chlorides are found naturally in unpolluted waters, but are harmful to fish in high concentrations.

The natural salinity of river water in the Chesapeake Estuary is 9.5 to 11.0 mg/l of chloride; and the natural salinity of ocean water is 7,000 to 10,300 mg/l of chloride.

DISSOLVED SOLIDS

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances.

Many communities in the United States and in other countries use water supplies containing 2000 to 4000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated whereas they could not be in temperate climates. Waters

containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh water fish may range from 5,000 to 10,000 mg/l, according to species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids over 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l water has little or no value for irrigation.

Dissolved solids in industrial waters can cause foaming in boilers and cause interference with cleaness, color, or taste of many finished products. High contents of dissolved solids also tend to accelerate corrosion.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used in a substitute method of quickly estimating the dissolved soldids concentration.

pH, ACIDITY AND ALKALINITY

Acidity is produced by substances that yield hydrogen ions on hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures

and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the taste of the water. At a low pH water tastes sour. The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This fact is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are esthetic liabilities to any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousandfold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0, and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Enough irritation will cause severe pain.

TEMPERATURE

Temperature is one of the most important and influential water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development; warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

Chemical reaction rates vary with temperature and generally increase as the temperature is increased. The solubility of gases in water varies with temperature. Dissolved oxygen is decreased by the decay or decomposition of dissolved organic substances and the decay rate increases as the temperature of the water increases, reaching a maximum at about 30°C (36°F). The temperature of stream water, even during summer, is below the optimum for pollution-associated bacteria. Increasing the water

temperature increases the bacterial multiplication rate when the environment is favorable and the food supply is abundant.

Reproduction cycles may be changed significantly by increased temperature because this function takes place under restricted temperature ranges. Spawning may not occur at all because temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to destroy a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Given amounts of domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

When water temperatures increase, the predominant algal species may change from diatoms to green algae, and finally at high temperatures to blue-green algae, because of species temperature preferentials. Blue-green algae can cause serious odor problems. The number and distribution of benthic organisms decrease as water temperatures increase above 90°F, which is close to the tolerance limit for the population. This occurrence could seriously affect certain fish that depend on benthinc organisms as a food source.

The cost of fish being attracted to heated water in winter months may be considerable, due to fish mortalities that may result when the fish return to the cooler water.

Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a watercourse.

In general, marine water temperatures do not change as rapidly or range as widely as those of fresh waters. Marine and estuarine fishes, therefore, are less tolerant of temperature variation. Although this limited tolerance is greater in estuarine than in open water marine species, temperature changes are more important to those fishes in estuaries and bays than to those in open marine areas, because of the nursery and replenishment functions

of the estuary that can be adversely affected by extreme temperature changes.

ARSENIC

Arsenic is found to a small extent in nature in the elemental form. It occurs mostly in the form of arsenites of metals or as pyrites.

Arsenic is normally present in seawater at concentrations of 2 to 3 ug/l and tends to be accumulated by oysters and other shellfish. Concentrations of 100 mg/kg have been reported in certain shellfish. Arsenic is a cumulative poison with long-term chronic effects on both aquatic organisms and mammalian species, and a succession of small doses may add up to a final lethal dose. It is moderately toxic to plants and highly toxic to animals especially as AsH3.

Arsenic trioxide, which also is exceedingly toxic, was studied in concentrations of 1.96 to 40 mg/l and found to be harmful in that range to fish and other aquatic life. Work by the Washington Department of Fisheries on pink salmon has shown that a level of 5.3 mg/l of As2O3 for 8 days was extremely harmful to this species; on mussels, a level of 16 mg/l was lethal in 3 to 16 days.

Severe human poisoning can result from 100 mg concentrations, and 130 mg has proved fatal. Arsenic can accumulate in the body faster than it is excreted and can build to toxic levels from small amounts taken periodically through lung and intestinal walls from the air, water and food.

Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. Although very low concentrations of arsenates may actually stimulate plant growth, the presence of excessive soluble arsenic in irrigation waters will reduce the yield of crops, the main effect appearing to be the destruction of chlorophyll in the foliage. Plants grown in water containing one mg/l of arsenic trioxides showed a blackening of the vascular bundles in the leaves. Beans and cucumbers are very sensitive, while turnips, cereals, and grasses are relatively resistant. Old orchard soils in Washington that contained 4 to 12 mg/kg of arsenic trioxide in the top soil were found to have become unproductive.

VANADIUM

Metallic vanadium does not occur free in nature, but minerals containing vanadium are widespread. Vanadium is found in many soils and occurs in vegetation grown in them. Vanadium adversely effects some plants in concentrations as low as 10 mg/l.

Vanadium as calcium vanadate can inhibit the growth of chicks, and in combination with selenium increases mortality in rats. Vanadium appears to inhibit the synthesis of cholesterol and accelerate its catabolism in rabbits.

Vanadium causes death to occur in fish at low concentrations. The amount needed for lethality depends on the alkalinity of the water and the specific vanadium compound present. The common bluegill can be killed by about 6 ppm in soft water and 55 ppm in hard water when the vanadium is expressed as vanadryl sulfate. Other fish are similarly affected.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

CADMIUM

Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment as practiced in the United States does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 ug/day of cadmium.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants, and up to 29,500 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

RADIOACTIVITY

Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism:

humans, fishes, and invertetrates. Beyond the obvious fact that including they emit ionizing radiation, radioactive wastes are similar in many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts. Plants and animals, to be of any significance in the cycling of radionuclides in the aquatic environment, must accumulate the radionuclide, retain it, be eaten by another organism, and be digestible. However, even if an organism accumulates and retains a radionuclide and is not eaten before it dies, the radionuclide organisms "biological cycle" through will enter the material into its elemental organic dead decompose the components. Plants and animals that become radioactive in this biological cycle can thus pose a health hazard when eaten by man.

Aquatic life may receive radiation from radionuclides present in the water and substrate and also from radionuclides that may acquire Humans tissues. within their accumulate radionuclides through many different pathways. Among the most important are through drinking contaminated water and eating fish and shellfish that have concentrated nuclides from the water. Where fish or other fresh or marine products that accumulated radioactive materials are used as food by humans, the concentrations of the nuclides in the water must be further restricted, to provide assurance that the total intake of radionuclides from all sources will not exceed the recommended levels.

In order to prevent unac eptable doses of radiation from reaching humans, fish, and other important organisms, the concentrations of radionuclides in water, both fresh and marine, must be restricted.

CONCLUSION

In view of the data presented above, it is judged that all of the mentioned waste constituents generated in the phosphate industry should be identified as pollution parameters as defined in the Federal Water Pollution Control Act Amendments of 1972.

In the paragraphs above, the harmful characteristics are given of all the parameters that are encountered in the phosphate manufacturing point source category. Table 11 summarizes the parameters found for each chemical.

Although many parameters appear in the waste streams from these plants, only those primary parameters signified by "x" need be used to set effluent standards.

The remaining parameters signified by zeros are adequately treated if the primary parameters are so treated.

TABLE 11

WASTE WATER CONSTITUENTS OF PHOSPHATE CATEGORY

| | | | | | | Parameter | eter | | | | |
|------------------------------------|-------------|------------|------------|-----------|---|-----------|-----------|------|----|----|-------|
| Chemical | | | | | | | | | | | |
| | TSS | PO4 PO3 | SO4 SO3 | F S1F6 | ជ | TDS | low pH | Heat | P4 | As | Ra, u |
| 0.00 | * | * | 0 | × | | 0 | 0 | 0 | × | 0 | • |
| 14 0 162 | | c | | | | 0 | 0 | 0 | 0 | 0 | |
| н ₃ Р0 ₄ | | , , | | | | 0 | 0 | • | 0 | | - |
| P ₂ 05 | | | • | | | 0 | 0 | 0 | 0 | 0 | |
| P ₂ S ₅ | > | × | | | С | 0 | × | 0 | • | × | |
| PC13 | < × | × | | | 0 | 0 | × | | 0 | 0 | |
| ruci3 | | 0 | | | | 0 | 0 | 0 | 0 | | |
| Na5 ² 3 ⁰ 10 | × | × | | 0 | | 0 | 0 | 0 | 0 | | |
| Cahru4 (reed grade) | | | | | | 0 | 0 | 0 | 0 | | |
| CaHPU4 (1000 grade) | , | | | | | | | | | | |

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

INTRODUCTION

Section V of this report quantitatively discussed the specific water uses in the phosphate industry and the raw wastes from this industry before control and/or treatment of these wastes. Section VI identified the constituents of the raw wastes which are classified as pollutants. Table 11 summarizes the pollutant constituents found as raw wastes in each of the three segments of the industry.

Two major observations may be made from table 11:

- 1. Classical sanitary engineering practices that treat effluents containing organic material or that are aimed at reducing biological oxygen demand are inapplicable to the phosphate manufacturing industry, where such pollutant constituents are usually very low and not a significant factor. Hence, control and treatment of the wastes in this industry are of the chemical and chemical engineering variety, and include neutralization, pH and chemical engineering variety, ionic reactions, filtration, control, precipitation, ionic reactions, filtration, centrifugation, ion exchange, demineralization, evaporation and drying.
- 2. A limited number of pollutant constituents characterizes the entire industry, crossing the lines between segments of the industry. Hence, the control and treatment techniques should be similar throughout the industry.

In this section of the report, the control and treatment technology is discussed in considerable detail. Much of this discussion is based on observed actual abatement practice in the industry and the accomplishments of independently verified sampling data of plant effluents.

IN-PROCESS CONTROLS

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices.

Segregation of Water Streams

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

- 1. non-contact cooling water
- 2. contact cooling water
- 3. process water
- 4. washings, leaks and spills
- 5. incoming water treatments
- cooling tower blowdowns
- 7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams with large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been compromised.

In general, plant effluents can be segregated into:

- 1. Non-contaminated Cooling Water. Except for leaks, non-contact water has no waste pickup. It is usually high volume.
- 2. Process Water. Usually contaminated but often small volume.
- 3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with a smaller contaminated process and auxiliary streams before full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower.

In the phosphorus chemicals industry, many plants have accomplished the desired segregation of water streams, often by a painstaking rerouting of sewer lines which have existed for many years. Among these plants which are notable in this respect are Plants 003, 037, 042, 075, and 182.

Recycle of Scrubber Water

The widespread use of water for scrubbing of tail gases in this industry has unfortunately led to many examples where the use of once-through scrubber water is the method of operation. However, there are several plants notable in this respect which recycle scrubber water from a sump, thus satisfying the scrubber water flow rate demands (on the basis of mass transfer considerations) while retaining control of water usage. These notable plants are TVA (Muscle Shoals, Alabama), and Plants 003 and 182.

Recycle of scrubber water permits the subsequent treatment of much smaller quantities of waste water with much higher concentrations of polluting constituents. Both these attributes make waste water treatment more economical, and in some cases, more efficient, from a removal viewpoint.

Dry Dust Collection

A drastic reduction in the aqueous waste load may be made by replacing wet scrubbing systems with baghouses, or alternatively, by placing cyclone dust collectors upstream of wet scrubbers. This approach is feasible because baghouses have recently been improved in design to the point where operation and maintenance costs are not excessive, where solids collection efficiences exceed those of wet scrubbers, and where operating temperature ranges have been extended with high-temperature media develop-Dry collected solids may be returned to the product stream, provided that a separate collector is installed for each This is a change in approach for the typical multiproduct phosphate plant, since conventional practice has been to centralize the collection and treatment functions across product lines. With dry separate collection, the product recovered may significantly contribute to alleviating the operating cost of the collectors.

Plants in this industry which are notable in this respect in having at least some dry dust collection include Plants 003, 006, 042, 119, and 182.

Housekeeping and Containment

Containment and disposal requirements may be divided into several categories:

- minor product spills and leaks
- 2. major product spills and leaks
- 3. upsets and disposal failures
- 4. storm water runoff
- pond failures
- 6. vessel and container cleanout

Minor Spills and Leaks

There are minor spills and leaks in all industrial chemical manufacturing operations. Pump seals leak, hoses drip, equipment is washed down, pipes and equipment leak, valves drip, tank leaks solids spill and so on. These losses are not going to be eliminated. They can be minimized and contained. In some cases the products are valuable; in other cases, personnel safety and prevention of corrosion may be paramount.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or types of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques employ the use of drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

Of special importance in the phosphorus consuming subcategory of the industry is the containment of phossy water from phosphorus transfer and storage operations. While displaced phossy water is normally shipped back to the phosphorus-producing facility, current practice in phosphorus storage tanks is to maintain a water blanket over the phosphorus for safety reasons. Make-up water is added resulting in the overflow of excess water.

This method of level control is unacceptable since it results in the discharge of phossy water. One way to ensure zero discharge is to install an auxiliary tank to collect phossy water overflows from the phosphorus storage tank; this system can be closed-loop by reusing this phossy water from the auxiliary tank as make-up for the main phosphorus tank. This scheme preserves the positive safety features of the existing level control practice and also safeguards against inadvertent large discharges resulting from leaky or misadjusted water make-up valves.

Major Product Spills and Leaks

These are catastrophic occurrences with major loss of product, tank and pipe ruptures, open valves, explosions, fires, and earthquakes.

No one can predict, plan for, or totally avoid these happenings, but they are extremely rare. Probably the most common of these rare occurrences is tank or valve failures. These can be handled with adequate dikes able to contain the tank volume. All acid, caustic, or toxic material tanks should be diked to provide this protection. Other special precautions may be needed for flammable or explosive substances. Plant 037 is a prime example where product tanks and transfer pumps have been systematically diked for containment of spills.

Upsets and Disposal Failures

In many processes there are short term upsets. These may occur during startup or shutdown or during normal operation. The phosphorus consuming subcategory and the phosphate subcategory of this industry may be more vulnerable to this type of upset since so many of the processes are batch-type operations with much more

direct operator control then the large-scale automated continuous processes typically found in the chemical industry.

These upsets represent a small portion of overall production but they nevertheless contribute to waste loads. The upset products should be treated, separated, and largely recycled. In the event that this can not be done, they must be disposed of.

One very special problem in the phosphorus consuming subcategory is the inadvertent spill of elemental phosphorus into a plant sewer line. Past practice has been to let it remain in the sewer and ensure a continuous water flow to prevent fire. There has been general reluctance to clean it out since phosphorus burns when exposed to air. With this practice, of course, all water flowing in that sewer from that time on becomes contaminated with phosphorus.

Provisions can be made for collecting, segregating and bypassing such phosphorus spills. One method is the installation of a trap of sufficient volume just downstream of reaction vessels, with appropriate installations and valving to enable the bypass of that trap after a spill has occurred and the offline removal and cleaning of the trap (with safe disposal of the phosphorus).

Stormwater Runoff

The phosphates segment of this industry is characterized by the handling, storing, conveying, sizing, packaging and shipping of finely-divided solid products. Typically, a phosphate plant has all the exterior surface of buildings, equipment and grounds covered with dusts. An area of concern is the pickup of these solids by stormwater either as suspended solids or as dissolved solids. Of course, washing down of these dusts is not acceptable; the dry solids must be collected. Where possible, the solids may be returned to appropriate process streams. Where purity requirements prohibit this return, adequate means for safe disposal of solid wastes must be provided.

Plants 003, 042 and 182 are examples of plants which have positive continual cleanup programs for solids, which minimize stormwater runoff. Most plants (with considerable credit to air pollution abatement practices) have also minimized the quality of airborne dusts.

The very practice of process water segregation discussed previously has led to the direct discharge of stormwater without treatment. Little is known from a quantitative standpoint about the severity of this problem in the phosphates segment of the industry, or to what extent containment and treatment of stormwater is required. In the phosphorus manufacturing segment of the industry, where large quantities of dusts are handled, plant 159 collects approximately 10 kg/kkg (20 lb/ton) in a settling pond for stormwater and non-contact cooling water.

may be the retically calculated as a function of pH (or of Ca:P

Pond Failures

Unlined ponds are the most common treatment facility used by the industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances.

Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside, or, more likely, the nearest body of water. Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control.

Good effluent control may be gained by a number of methods, including:

- Pond and diking should be designed to take the anticipated rainfall; smaller and deeper ponds should be used where feasible.
- Control ponds should be constructed so that drainage from the surrounding area does not innundate the pond and overwhelm it.
- Substitution of smaller volume (and surfaced) treatment tanks, coagulators, or clarifiers can reduce rainfall influx and leakage problems.

Vessel and Container Cleanout

One common characteristic of the phosphorus consuming subcategory of the industry is the planned accumulation of residues in reaction vessels and stills, with infrequent shutdowns to clean and remove these residues. In many cases, the residues are washed down with firehoses and the wastes discharged. This practice is clearly unacceptable. One alternative is the diking of the area with collection and treatment of the aqueous wastes, in conjunction with an effort to minimize the quantity of washwater.

A similar situation exists with regard to the cleaning of returnable containers (drums, tank trucks and tank cars) before reuse. Since these are routine operations, procedures and facilities must be made available for minimizing the quantity of waste water and for the collection and treatment of this waste water.

Monitoring Techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to waste water analysis. Acidity and alkalinity are detected by pH meters, often installed in-line for continuous monitoring and control.

Dissolved solids may be estimated by conductivity measurements, suspended solids and turbidity and specific ions by wet chemistry and colorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most commonly used in-line monitoring instrument. Spills, washdowns and other contributions become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

Monitoring and control of harmful materials such as phosphorus and arsenic is often so critical that batch techniques may be used. Each batch can be analyzed before discharging. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. This follows from the fact that most dissolved solids are rather inert. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates, and other low ion concentrations.

Summary

The preceding narrative described general treatment practices and in-plant controls. The following discusses specific abatement measures recommended for each subcategory.

tracione Ton Exchange Systems

TREATMENT OF WASTE WATERS IN THE PHOSPHORUS SUBCATEGORY

Neutralization of Acidic Waste waters

Virtually every manufacturing process in the phosphate industry results in a raw waste load of significant acidity. In some cases, advantage is taken of the availability of alkaline waste to at least partially neutralize the acid waste streams.

At phosphorus producing plants, some neutralization of acidic calciner scrubber liquor is achieved by the alkaline slag or by the slightly alkaline slag quench liquor (see Table 7). At TVA, the slag is granulated by quenching with a high-velocity jet of calciner scrubber liquor plus process cooling water. The granulated slag (with its large surface area) effectively neutralizes the acidic liquors. At plants not granulating slag (Plants 028 and 181), the slightly alkaline slag quench liquors are mixed with the highly acidic scrubber liquors for partial neutralization.

Except for this one case where granulated slag is available, lime or limestone neutralization of acid waste streams is standard practice in this industry as observed at Plants 003, 006, 028, 159, 181, and 182. The relative chemical costs reported by Downing, Kunin and Polliot (28), listed in Table 12, show that limestone or lime are far and away more economical than other neutralizing materials. Limestone is the lower cost material (approximately \$11/kkg (\$10/ton)) but suffers the disadvantages of slower reaction and lower obtainable pH than lime. Lime costs approximately \$22/kkg (\$20/ton).

With the exception of hydrochloric acid from PCl3 and POCl3 manufacturing facilities, every acid waste in the phosphorus chemicals industry forms insoluble or slightly soluble calcium salts when treated with lime:

| Acid | Calcium Salt | Solubility*, mg/l |
|------------|-----------------------|--------------------|
| H3PO4 | Ca (H2PO4) 2.H2O, MCP | 18,000 |
| -,, - | CaHPO4.2H2O, DCP | 200 |
| | Ca3 (PO4) 2, TCP | 25 |
| HF, H2SiF6 | CaF2 | 16 |
| H2SiO3 | casio3 | 95 |
| H2SO4 | CaSO4.2H2O | 2,410 |
| H2SO3 | Caso3.2H2O | 43 |
| H3PO3 | 2 CaHPO3.3H2O | (Slightly Soluble) |

^{*}Between 17°C and 30°C.

It is readily apparent that lime treatment (with excess lime) not only neutralizes acidic waste waters from the phosphate manufacturing industry, but also demineralizes most waste waters by precipitating calcium salts. This then produces a solid waste which may be disposed of by landfilling.

TABLE 12 Relative Chemical Costs for Neutralizing Acid Wastes Source: Downing, Kunin and Polliot⁽²⁸⁾

| | Relative Cost per | Relativ | e Weight d Per Pou | Alkali ind Acid | | ive Cost ound Acid | 1 |
|-------------------------------------|----------------------|--------------------------------|-----------------------|--------------------------------|--------------------------------|-----------------------|--------------------------------|
| NEUTRALIZING MATERIAL | Pound Alkali* | H ₂ SO ₄ | нст | H ₃ PO ₄ | H ₂ SO ₄ | нст | H ₃ PO ₄ |
| Lump limestone, high Ca | 1.16 | 110 | 148 | 165 | 128 | 172 | 191 |
| unp limestone, dolomitic | 1.00 | 94 | 127 | 141 | 94 | 127 | 141 |
| Pulv. limestone, high Ca | 1.59 | 110 | 148 | 165 | 175 | 235 | 262 |
| Pulv. limestone, dolomitic | 1.37 | 94 | 127 | 141_ | 129 | 174 | 193 |
| lydrated lime, high Ca | 3.06 | 79 | 107 | 119 | 242 | 327 | 364 |
| ydrated lime, dolomitic | 2.50 | 65 | 87 | 98 | 162 | 217 | 245 |
| Pebble lime, high Ca | 2.07 | 60 | 80 | 90 | 124 | 166 | 186 |
| Pebble lime, dolomitic | 1.87 | 54 | 73 | 81 | 101 | 136 | 151 |
| Pulv. quicklime, high Ca | 2.18 | 60 | 80 | 90 | 131 | 174 | 196 |
| Pulv. quicklime, dolomitic | 1.97 | 54 | 73 | 81 | 106 | 144 | 159 |
| Sodium bicarbonate | 20.65 | 173 | 233 | 260 | 3570 | 4810 | 5360 |
| | 13.08 | 119 | 160 | 179 | 1560 | 2090 | 2340 |
| Soda ash | 9.96 | 164 | 220 | 246 | 1630 | 2190 | 2450 |
| Caustic soda (50%) | 5.90 | 35 | 47 | 53 | 207 | 277 | 31: |
| Ammonia (anhyd.) Magnesium oxide | 3.90 | 42 | 56 | 63 | 164 | 218 | 246 |

^{*}Delivered cost including freight.

The effectiveness of the control specified in the preceding paragraphs is summarized in Table 13 for four plants (TVA, 181, 028 and 159). Data for plants 028 and 159 were taken from Tables 14 and 15, which include a complete analysis on the intake and effluent waters.

Removal of Anions (Except Chlorides) From Acidic Wastes

Neutralization of acid waste waters with lime also precipitates the calcium salts of all acid wastes in this industry (with the exception of hydrochloric acid from PCl3 and POCl3 manufacture). This treatment is widespread throughout the phosphate manufacturing industry, and represents a class of treatment technology which has widespread validation and demonstration at plant-scale installations.

Other technologies for removing dissolved solids (except chlorides) are also presented in this section, with a somewhat lesser degree of full-scale validation than lime treatment.

Treatment of Acidic Fluoride Wastes

Acidic fluoride wastes are generated by the phosphorus producsegment of the industry and by the defluorination of wet-process acid in the manufacture of animal feed grade calcium phosphates. These waste waters containing large quantities of hydrofluoric, fluosilicic and silicic acids are neutralized with lime (which breaks down H2SiF6 at high pH) to precipitate calcium fluoride and gelatinous hydrated silica. Lime treatment is standard operating technology at Plants 128, 159, 181 and 182.

Like lime treatment of phosphoric acid, lime treatment of acidic fluoride wastes is enhanced by the decreased solubility of CaF2 at high pH:

$$CaF2(s) \longrightarrow Ca+2 + 2F \longrightarrow Ca+2 + 20H + 2HF$$

The equilibrium is driven to the far left by the addition of excess lime. The theoretical solubility of CaF2 may be calcined in much the same manner as outlined for Ca3 (PO4)2, using the ionization constant of HF and the pure water solubility data for CaF2.

There has been recent commercial interest in recovering the fluoride values in acidic waste waters. Two commercial processes have been developed to manufacture hydrofluoric acid and one to manufacture synthetic cryolite for the aluminum industry.

Removal of Suspended Solids

The raw waste streams from the phosphorus producing segment and from the phosphate subcategory of the industry contain considerable quantities of suspended solids. Moreover, the

would lower the PCI3 vapor product and account double the

TABLE Summary of Control & Treatment Techniques at Phosphorus-Producing Plants (For Process Waters Other Than Phossy Water)

| | TSS | Total Acidity (Alkal- inity) | TDS | Fluoride | Sulfate | Total Phosphate |
|------------------------------------------------------------------------------|------------------------|---------------------------------------|-------------------|--------------------------|------------------------|------------------------|
| Raw Waste Loads (from Sec. ¥) Kg/Kkg lb /ton | 42.5 85 | 54.5 109 | : | 53.5 107 | 111 222 | 25 50 |
| Waste Discharged, Kg/Kkg: TVA Plant 181 Plant 028 (Net) Plant 159 (Gross) | 0 0 0.5 0.5 | 0 0 1 (12) | 0 0 4 22 | 0 0 0.1 0.04 | 0 0 2 3 | 0 0 0.2 0.8 |
| Waste Discharged, 1b /ton: TVA Plant 181 Plant 028 (Net) Plant 159 (Gross) | 0 0 1 1 | 0 0 3 (24) | 0 0 9 45 | 0 0 0.2 0.07 | 0 0 4 7 | 0 0 0.4 1.6 |
| Control & Treatment Efficiency, Per Cent: TVA Plant 181 Plant 028 Plant 159 | 100 100 99 99 | 100 100 - | 100 100 - | 100 100 99+ 99+ | 100 100 98 97 | 100 100 99 97 |

TABLE 14 - Effluent from Plant 028 (Discharge No. 001)

Effluent Flowrate = 103-200 1/kkg (24,700 gal/ton)

Notes:
1. This Discharge is from Cooling Water and Dust Collector Water.
2. There is Zero Discharge of Phossy Water and Calciner Scrubber Water

| | Water | & Waster | water Anal | ysis | Net Ef | fluent /Kkg | | fluent b /ton |
|------------------------------|-------------------------|----------|---------------------------|--------------------------|---------------|--------------------------|---------------|--------------------------|
| Constituent | Units | Intake | Effluent Plant Data | Effluent Ind. Data | Plant Data | Inde- pendent Data | Plant Data | Inde- pendent Data |
| рН | - | - | 7.3-9 5 | 7.55 | - | - | • | - |
| Turbidity | FTU | 26 | 32 | 30 | - | - | - | - |
| Conductivity | unhos cm | 359 | 403 | 300 | - | - | - | |
| TSS | mg/l | 15 | 15 | 20 | - | 0.5 | 0 | 1 |
| TDS | mg/1 | 160 | 202 | 176 | 4 | 2 | 9 | 3 |
| CaCO3 Alkalinity | mg/l | 116 | 110 | 130 | (-1) | 1 | (-1) | 3 |
| CaCO ₃ Acidity | mg/1 | - | - | - | - | - | - | - |
| Chloride | mg/1 | <0.1 | 4.1 | -8 | 0.4 | 0.8 | 0.9 | 1.6 |
| Fivoride | mg/1 | 0.19 | 1.14 | 0.87 | 0.10 | 0.07 | 0.20 | 0.14 |
| Sulfate | mg/1 SO ₄ | 6.4 | 13.8 | 26 | 0.8 | 2.1 | 1.5 | 4.1 |
| COD | mg/1 | 2.0 | 53.5 | 25 | 5.3 | 2.4 | 10.6 | 4.8 |
| Total Hardness | mg/1 | 116.7 | 129.7 | 160 | 1 | 4 | 3 | 8 |
| Total Phosphate | mg/1 PO ₄ | 1.2 | 2.4 | - | 0.13 | 2 - | 0.25 | |
| Ortho Phosphate | mg/1 PO ₄ | 1.2 | 2.4 | 2.9 | 0.1 | 2 0.18 | 0.25 | 0.35 |

TABLE 15 Effluent from Plant 159

Notes: 1. There is Zero Discharge of Phossy Water
2. These data are Plant Data, Not Independently Verified

Effluent Flowrate = 36,100 1/kkg (8,640 gal/ton)

| | | Water & water A | | Gross Ef Quanti | | Net Eff1 Quanti | |
|---------------------------------|-------------------------|-------------------|----------|--------------------|---------|--------------------|----------|
| Constituent | Units | Treated Intake | Effluent | Kg/kkg | lb /ton | Kg/kkg | 1b /ton |
| pH | _ | 7.5 | 8.0-8.5 | - | - | - | - |
| Turbidity | FTU | <1 | 11 | - | - | - | - |
| Conductivity | <u>µmhos</u> | 966 | 898 | - | - | - | - |
| TSS | mg/1 | 11 | 15 | 0.54 | 1.08 | 0.14 | 0.29 |
| TDS | mg/1 | 617 | 620 | 22.4 | 44.8 | 0.11 | 0.22 |
| CaCO ₃ Alkalinity | mg/l | 358 | 323 | 11.7 | 23.4 | (-1.3) | (-2.6) |
| CaCO ₃ Acidity | .mg/1 | - | | - | - | - | - |
| Chloride | mg/1 | 50 | 53 | 1.9 | 3.8 | 0.11 | 0.22 |
| Fluoride | mg/1 | 0.84 | 1.01 | 0.04 | 0.07 | 0.0061 | 0.0122 |
| Sulfate | mg/1 S0 ₄ | 91.5 | 90.0 | 3.2 | 6.5 | | (- 0.103 |
| COD | mg/1 | - | 6 | - | 0.2 | 0.22 | 0.43 |
| Total Hardness | mg/1 | 465 | 468 | 16.9 | 33.8 | 0.11 | 0.22 |
| Total Phosphate | mg/1 PO ₄ | 18.0 | 22.4 | 0.8 | 1.6 | 0.16 | 0.32 |
| Ortho Phosphate | mg/1 PO ₄ | 15.9 | 19.3 | 0.7 | 1.4 | 0.12 | 0.24 |

chemical treatment of acidic wastes described in the previous section produced in many instances additional suspended solids.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids. They are in use at Plants 006, 028, 119, 159, 181 and 182. Removal of suspended solids generates a solid waste effluent which must be disposed of by landfilling.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics can be cleared up in one or two small ponds; others with heavier suspended solids loads and/or slower settling rates may require 5 to 10 large ponds. Most settling ponds are unlined, but the technology exists for lined ponds.

Although not as widely used as settling ponds, tanks and vessels are also employed for removal of suspended solids in the phosphate manufacturing industry. They are in use at TVA (Muscle Shoals, Alabama) and at Plants 003, 006, 028 and 159.

Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds) should lead to increasing use of vessels and tanks in the future, especially where a plant is short of available land for settling ponds.

Filtration equipment, such as plate-and-frame pressure filters, pressure or vacuum leaf filters, rotary vacuum filters, and pressure tubular filters, has been widely used in the chemical and waste treatment field for many years. The batch-type filters find most use in polishing applications to completely remove small quantities of suspended solids, since the labor-intensive blowdown operation is dependent on cake volume. These filtrations are common for collection of undesirable solid wastes, such as arsenic sulfide from food grade phosphoric acid. Continuous rotary vacuum filters find general applicability in dewatering sludges with high concentrations of solids. Sand bed filtration also finds increasingly widespread use.

Filtration is in use at Plants 006, 075 and 119. In general, filtration is not economically attractive for huge quantities of waste water (except for sand bed filtration). It is usually preceded by a gravity thickening operation so that it treats the thickened sludge which is only a small volumetric percentage of the total waste water flow.

Centrifugation, in use at Plant 003 and at the TVA installation, is an alternative means for mechnical dewatering of relatively low flow rate sludges, and has made major recent inroads into the domestic waste water treatment field. The continuous solid-bowl centrifuge, as its name implies, provides for continuous removal of the cake, and its design reaches a compromise between solids recovery and cake dryness. The basket solid-bowl centrifuge, on and discharges cake intermittently, the other hand, cake-drying portions of the cycle may be and dewatering separately controlled. Perforated-bowl centrifuges are really machines offer the The solid-bowl centrifugal filters. significant advantage over filters that blinding of a medium is removed as a problem area.

Dewatering of Lime-Precipitated Phosphates

Although (as previously discussed) lime can be used to effectively precipitate phosphates from solution to reduce the concentration to 0.3 mg/l or less (as PO4), the lime-precipitated phosphates do not dewater readily, but form a water-trapping gel structure. After 24 hours of settling, clarified effluents still may have 15 to 50 mg/l of suspended solids. This condition can be significantly improved by increasing the detention time to 7 days, but the suspended solids content may still be 5 mg/l or greater. In the phosphate manufacturing industry, settling ponds with 7 days or longer detention times (equivalent to an overflow rate of 420 1/day/m² (10 gpd/ft²) at a nominal depth of 3 m (10 settling the It has been reported that are used. ft)) initial the dependent on are strongly characteristics An initial concentration of concentration of phosphate ion. 75,000 mg/l resulted in a compacted settled slurry density 3 to 5 times higher than if the initial concentration was 1,500 mg/l.

Where sufficient land area for large settling ponds is not available, average removal efficiencies of 80 to 95 percent have been obtained with mechanically raked gravity thickeners. A typical thickener design has a 2-hour detention time and an overflow rate of 42,000 1/day/m² (1,000 gpd/ft²).

Synthetic organic, water-soluble, high molecular weight polyelectrolytes have achieved great success in flocculation and clarification and in sludge conditioning before centrifugation or filtration. A polymer dosage of 0.05 kg per kkg of dry sludge solids (0.1 lb/ton), or about 1 mg/l of a 2 percent slurry, may achieve 85 percent removal of suspended solids at a detention time of 2 hours, with a 12 percent solids content in the thickened sludge. If this thickened sludge were then vacuum filtered, a cake of 30 percent solids could be obtained with a solids content in the filtrate of 0.5 mg/l of less.

The following may be a typical performance chart for an influent sludge containing 100 liters of water:

| | Volume of Water, liters | Susp <i>e</i> nded Kg | Solids Percentage |
|---------------------|-------------------------|--------------------------|----------------------|
| Influent | 100 | 2.56 | 2.5% |
| Thickener Overflow | 84 | 0.38 | 0.45% |
| Thickener Underflow | 16 | 2.18 | 12% |
| Filter Cake | 5.1 | 2.18 | 30% |
| Filtrate | 10.9 | 5 x 10-16 | 0.5% |

The dewatered cake, containing 85 percent of the original solids, may be landfilled. The filtrate, when combined with the thick-ener overflow, would consist of 95 percent of the original water quantity and would have a suspended solids concentration of 4,000 mg/l.

A much clearer effluent could be obtained, of course, if all of the influent waste water were directly filtered. Such is the practice at Plant 006, which achieves an average phosphate removal efficiency of 95 percent.

Mechanical dewatering of lime precipitated phosphates by centrifugation was attempted, but it proved unsuccessful because the highly thixotropic cake plugged the solids-removal screw.

Because an excess of lime is used in the precipitation of the phosphates, the effluent from the ponds or from mechanical thickening and dewatering would have a high pH, typically 10 to 11. This effluent could be partially carbonated (with CO2) to reduce the pH to 8.0 to 8.5 before discharge, with another filtration step to remove the calcium carbonate precipitate. Alternatively, it has been shown that subsequent activated sludge treatment of high pH waste water at municipal treatment plants lowers the pH due to biologically-released CO2 from the oxidation of organic material.

Treatment Alternatives

There were two treatment alternatives considered for this subcategory. The first alternative is the treatment currently employed by 90 percent of the industry. This includes complete recycle of phossy water, evaporation of some process water, lime treatment, and sedimentation of the remaining water prior to discharge. The second alternative practiced by 10 percent of the industry, involved 100 percent recycle of all process water.

TREATMENT OF WASTE WATERS IN THE PHOSPHORUS CONSUMING SUBCATEGORY

Control and Treatment of Phossy Water at Phosphorus Producing Plants

Because of harmful effects of elemental phosphorus in small concentrations in waste water, and because complete removal of the phosphorus from the water is not practical, it is a universal practice at phosphorus-producing plants to reuse the phospy water after treatment (which is required to remove other constituents in the waste water which would otherwise build up to concentration).

Barber (5) discusses several methods which have been tried experimentally to remove elemental phosphorus from phossy water. Among these methods were chlorination, which was tried more than 20 years ago and which was discarded at that time because "accurate chlorinator control was found to be impractical." With the development of chlorine analyzer-controllers for municipal waste water treatment, however, it appears that chlorination deserves another trial. Air oxidation was attempted, but the reaction was far from complete, leaving 14 to 37 percent of the original colloidal phosphorus unoxidized. Filtration of the colloidal phosphorus was investigated but found impractical. As a result of these discouraging results, the industry has adopted the route of containment and re-use rather than treatment and discharge.

At the TVA Muscle Shoals plant, a commercial flocculant, at a concentration of 40 mg/l, is employed to settle both the phosphorus and the suspended solids. Using a clarifier, the system removes 92 to 93 percent of both the phosphorus and the suspended solids as phosphorus sludge underflow (which is only 2 percent of the waste water volume). The presence of suspended solids is necessary for efficient removal by this method.

The underflow from the clarifier may be treated as other phosphorus muds or sludges are treated. The sludge may be gravity thickened and/or dewatered by centrifugation or filtration. The sludge, thickened sludge, or sludge cake (with respectively lower moisture contents) may then be neat-dried in an inert atmosphere using the process byproduct carbon monoxide as fuel. Elemental phosphorus (nominally 40 to 65 percent of the "solids" in the sludge) are recovered. The remaining nonvolatile solids contain no elemental phosphorus and can be safely disposed of or recycled to the feed preparation section of the phosphorus manufacturing plant.

The clarifier overflow, containing only 7 or 8 percent of the original phosphorus and suspended solids, may then be recirculated to the phosphorus condenser sump and to other areas where water contacts phosphorus. However, because the phospy water accumulates dissolved salts (mainly fluorides and phosphates, see Table 7), about 6 percent of the clarified water must be bled off

and discharged. In addition to suspended solids and dissolved solids, this bleed contains 120 mg/l of elemental phosphorus, equivalent to 0.4 kg/kkg, or 0.08 pound per ton, of product.

At Plant 181, a different approach is taken towards phossy water wastes. Very large lagoons not only reduce the concentration of suspended solids in the phossy water, but also serve to slowly oxidize much of the elemental phosphorus to phosphates. Subsequent lime treatment of the lagoon overflow (after combining with other waste water streams) precipitates not only the phosphates but also the fluorides in the water, thereby reducing the quantity of dissolved salts so that the water may be reused without a bleed. At this plant, the waste streams may be combined since all wastes are recycled without discharge.

A slightly different approach is taken at Plant 128. The phossy water is combined in a closed treatment and recycle system with calciner scrubber liquor. After settling of suspended solids and partial oxidation of phosphorus in a pond, lime treatment is used to precipitate dissolved phosphates and fluorides. Upon subsequent settling, the clarified (but still phossy) water is reused as calciner scrubbing water. Fresh make-up is used for the phosphorus condenser. The key to this scheme, which results in zero discharge of phossy water, is that the quantity of water vaporized in the calciner scrubber (in cooling the calciner tail gases) exceeds the quantity of phossy water in the raw waste load, so that fresh water may be continuously added to the loop without discharging any contaminated water.

Plant 159 achieves zero discharge of phossy water in a unique system. The completely segregated raw waste phossy water is sent to a clarifier in a manner similar to the TVA technique described above. The clarifier underflow of phosphorus sludge is treated in conventional ways, with complete return of the material to the process. The overflow from the clarifier is not recycled (as is the TVA practice, which requires a bleed discharge), but is sent to an evaporation pond.

In the approaches used by Plants 028 and 159, some or all of the phossy water is evaporated. This presents no hazard of elemental phosphorus, since it is very rapidly oxidized to phosphate as soon as the protective water is removed.

In summary, this study found three different ways that existing plants are achieving zero discharge of phossy water.

Treatment of Arsenic-Rich Residues

Arsenic-rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. The common disposal method is burial in a controlled area, as practiced at Plants 075, 119, 147 and 192.

The arsenic-rich liquid residue from the PCl3 distillation is more difficult to dispose of. At Plant 037 this residue is first treated with trichloroethylene, in which PCl3 is miscible but AsCl3 is not. The trichloroethylene is then water-washed to remove the arsenic-free PCl3 and the trichloroethylene is reused. The AsCl3-rich residue is then segregated and stored in drums for final disposal in an environmentally safe manner.

Treatment of Phosphoric Acid Wastes

The standard treatment of these wastes is by neutralization and/ or precipitation with lime as discussed for the phosphorus production subcategory. The final product of neutralization, in an excess of lime and in a considerable excess of water, is formed:

6 H3PO4 + 10 Ca (OH) $2 \rightarrow 9$ CaO.3 P2O5.Ca (OH) 2 + 18 H2O

Although this material is very insoluble, the reaction does not proceed to completion in practice unless a Ca/P mole ratio of at least 1.9 is reached. Moreover, the reactivity of the lime in precipitating the dissolved phosphate is strongly dependent on the lime source and the slaking conditions. It has been found that freshly slaked pebble quicklime can precipitate in excess of 97 percent of the phosphate, whereas commercial hydrated lime (calcium hydroxide) or freshly slaked ground quicklime only succeeded in a 73 to 80 percent precipitation efficiency under the same conditions.

A large body of literature has been developed in the lime treatment of domestic waste waters for phosphate removal. The study performed by Black & Veatch for EPA(31) summarizes the efforts that have been sufficiently demonstrated to be applied to current municipal waste water treatment projects. It is pointed out that the average concentration in domestic raw waste water is about 10 mg/l (expressed as elemental phosphorus). The domestic sources are about 1.6 kg (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents.

The existing practice achieves better than 90 percent removal of the phosphates from domestic waste water, reducing the concentration (expressed as PO4) from 30 mg/l to as low as 0.3 mg/l. At first glance, this seems to conflict with the fact that tricalcium phosphate (or hydroxylapatite) has a solubility of 25 mg/l (equivalent to 15 mg/l as PO4). However, in a large excess of lime, the pH is sufficiently high (10 to 11) to reduce the solubility of this salt of a strong base and weak acid. The equilibrium

 $Ca+3 (PO4) 2 (s) \longrightarrow 3Ca^2 + PO4^{-3} \longrightarrow 3Ca^{+2} + 2OH^{-} + 2HPO4^{-2}$

is driven to the far left (reducing phosphate solubility) by the addition of excess lime. The solubility of tricalcium phosphate

may be theoretically calculated as a function of pH (or of Ca:P ratio) using the ionization constants for H3PO4, H2PO4-1, and HPO4-2 in conjunction with a solubility product for tricalcium phosphate (which may be calculated from solubility data in pure water).

This phenomenon, substantiated by full-scale operating data as reported by Black & Veatch (31), is summarized below:

| рН | Phosphate Concentration of Filtered Effluent, mg/l |
|------|----------------------------------------------------|
| 9.0 | 5.7 |
| 9.5 | 1.4 |
| 10.0 | 0.6 |
| 10.5 | 0.3 |
| 11.0 | 0.2 |

The literature is replete with details of technology to achieve high removal efficiencies. (31-42) For example, thickened sludge recirculation to the neutralization tank has been found to seed the precipitation of calcium phosphate, resulting not only in better removal of dissolved phosphates but also in the growth of larger crystals for easier dewatering.

Although lime treatment of phosphates has been the predominant route, ferric chloride and alum have also been extensively used. Ferric salts are most effective in the 4 to 5 pH range and aluminum salts are most effective in the 5 to 6 pH range, as opposed to the 10 to 11 range for lime. The mole ratio of Fe/P or Al/P should be around 2.0, the same as the Ca/P ratio with lime treatment.

The use of lanthanum salts has recently been demonstrated to more effectively precipitate phosphates over a much wider pH range than calcium, ferric ion, or aluminum. The drawback is cost; the treatment system must recover and reuse the lanthanum.

Another process for phosphate removal is adsorption by activated alumina with subsequent stripping with caustic acid, and then regeneration of phosphate-free caustic by lime precipitation. Ion exchange has also been investigated.

One interesting process for phosphate removal is borrowed from a commercial process for HCl acidulation of phosphate rock. Phosphoric acid is recovered by solvent extraction, using C4 and C5 primary alcohols such as n-butanol and isoamyl alcohol. The chloride-free phosphoric acid is then extracted from the organic phase by water washing, the solvent is recycled, and the pure phosphoric acid may be concentrated by evaporation of water. This treatment method appears attractive for application to the food grade calcium phosphate waste streams. The suspended solids may be dissolved by HCl addition, and solvent extraction may be used to regenerate phosphoric acid for return to the process.

Treatment of Acidic Sulfite, Sulfate, and Phosphate Wastes

These acids are components of the waste streams from the phosphorus-consuming subcategory of the industry; and sulfuric acid is also a constituent of the wastes from the phosphorus production segment. The sulfurous and phosphorus acids may be partially oxidized prior to treatment to sulfuric and phosphoric acids.

The neutralization and precipitation of the slightly soluble calcium salts is exactly comparable to the treatment of acidic phosphate and fluoride wastes. The solubilities of calcium sulfite and of calcium phosphite are repressed by excess lime as in the previously discussed cases, but the solubility of calcium sulfate (a salt of a strong base and a strong acid) is not affected by ph.

Removal of Chlorides

Ion Exchange and Demineralization

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 mg/l or less.

An ion exchange may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge, and an exchangeable ion carrying an opposite charge. The inert matrix is usually crosslinked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

RSO3H + NaCl ≠ RSO3Na + HCl RCO2H + NaCl ≠ RCO2Na + HCl

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use basic group such as the amino family.

RNa3OH + NaC1 = RNa3C1 + NaOH

This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 16 gives the level of total dissolved solids that is achieved. Special ion exchange systems have been developed for treating high dissolved solids content (more than

The capital costs for small unlined ponds, with aleas ilon v. v.

TABLE 16. Water Quality Produced by Various Ion Exchange Systems

| Exchanger Setup | Residual Silica, mg/l | Residual Electrolytes,mq/l | Specific Resistance ohm-cm |
|---------------------------------------------------------------------------------------|-----------------------------|----------------------------|----------------------------|
| Strong acid cation | No silica | 3 | 500,000 |
| + weak-base anion Strong-acid cation | removal 0.01-0.1 | 3 | 100,000 |
| + weak-base anion + strong-base anion strong-acid cation + weak-base anion | 0.01-0.1 | 0.15-1.5 | 1,000,000 |
| + strong-acid cation + strong-base anion Mixed bed (strong- acid cation + | 0.01-0.1 | 0.5 | 1-2,000,000 |
| strong-base anion) Mixed bed + first | 0.05 | 0.1 | 3-12,000,000 |
| or second setup above similar setup as immediately above + continuous re- circulation | 0.01 | 0.5 | 18,000,000 |

1000 mg/liter total dissolved solids), minimizing regenerant chemicals costs.

Reverse Osmosis

thickening.

The phenomenon of osmosis has its explanation in thermodynamic equilibrium and free energy concepts. Essentially, when a semipermeable membrane separates a pure liquid and solution of dissolved material in the same liquid, there is a net migration of the pure liquid to the solution, driven by the free energy difference between the two sides of the membrane. Equilibrium is reached only when the liquids on each side of the membrane are of the same composition, or sufficient additional pressure is applied on the solution side of the membrane to counterbalance the osmotic driving force. Application of additional pressure on the solution side reverses the direction of osmotic flow through the membrane and results in concentration of the solution and migration of additional pure liquid to the pure liquid side. This is reverse osmosis. It may be looked at as pressure filtration through a molecular pore-sized filter.

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. Its weakness comes from the criticalness it has to blinding, plugging, and chemical attack. Acidity, suspended solids, precipitations, coatings, dirt, organics and other substances can make it inoperative. Membrane life is critical and unknown in many mediums.

With these restrictions there is little wonder that its industrial applications are few. Fortunately, the phosphorus chemicals industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500 mg/l to 20,000 mg/l) dissolved solids removal. Organics are usually absent, suspended solids are low and can be made low rather easily, acidity is easily adjusted, and the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

Evaporation Ponds

Plant 159 utilizes an evaporation pond for disposal of phossy water from phosphorus manufacturing. They may also be reasonably used for other waste water disposal where the waste water quantities are not overwhelming.

The size of an evaporation pond depends on the climatic differential between evaporation and rainfall:

Pond Area

| 2 2 min (1) ft (yr) 0.030 | ha/cu | m/day | (280 | acres/MGD) acres/MGD) acres/MGD) |
|---------------------------|-------|-------|------|----------------------------------------|
|---------------------------|-------|-------|------|----------------------------------------|

Evaporation ponds may be either unlined or lined, and should be diked. Use is often made of natural pits, valleys or ponds.

Conventional evaporation ponds are not, of course, among the useful treatments in areas where the rainfall exceeds the evaporation. However, surface aerators (commonly used for aerated lagoons in secondary treatment of organic wastes) can significantly increase the evaporation from a pond by increasing the water/air surface area.

Single-Effect and Multiple-Effect Evaporators

For the treatment of small waste streams, single-effect evaporators are characterized by low equipment costs and by inherent reliability, at the expense of high steam requirements. Conventional multiple-effect evaporators, with 2 to 6 effects, have somewhat higher capital costs, but require much less steam.

Evaporation is a technology, of course, that is aptly demonstrated throughout the chemicals process industry (although not extensively for the sole purpose of waste treatment), and as such meets the requirements of being currently available.

Refrigerated Condensers for PC13 and POC13

In the standard processes for manufacturing PC13 and POC13, the present industry practice is to use water cooled condensers to reflux the reaction vapors and to collect the product. Because the vapor pressure of PC13 is significantly high (boiling point 76°C (169°F)) at normal condensing temperatures, the raw waste load in the tail-gas water scrubbers contains rather large quantities of the hydrolysis products of PC13. The use of refrigerated condensers in place of the water-cooled condensers, or alternately, the use of cold traps downstream of the water-cooled condensers, would drastically reduce the amount of PC13 in the tail gas which subsequently becomes acid aqueous wastes:

| Temperature, °C | Temperature, oF | PCl3 Vapor Pressure, mm Hq(27) |
|------------------------|-------------------------------|-----------------------------------|
| -40 -20 0 +20 | -40 - 4 32 68 104 | 3 13 38 99 235 |
| +40 | 104 | |

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It is apparent that a condensing temperature below -20°C (-4°F) would lower the PCl3 vapor pressure by an order of magnitude over normal condensing temperatures and would virtually double the temperature driving force for heat transfer.

Refrigerated condensers are in current use (for POCl3 manufacture using air oxidation) at Plant 037.

Inert-Atmosphere Casting of P2S5

The present industry practice is to cast molten P2S5 product into shipping containers or into conical forms. When molten P2S5 is exposed to the atmosphere, it spontaneously ignites, forming P2O5 and SO2 which are subsequently water-scrubbed.

There are various state-of-the-art techniques available for casting either in an inert atmosphere or in vacuum, to eliminate this source of raw aqueous waste.

Treatment Alternatives

The treatment alternatives considered for the manufacture of phosphoric acid are additional treatment (the only discharges are from leaks and spills) and no discharge of any process waste water pollutants to navigable waters. The latter alternative involves tightened housekeeping and maintenance construction of dikes and dams around pumps, valves, and tanks; construction of sumps and sump pumps; lime treatment of leaks and spills; and landfill of the sludge. This is currently practiced by 10 percent of the industry.

There were two treatment alternatives considered for the manufacture of phosphorus pentoxide: no additional treatment and no process waste water discharge.

Three treatment alternatives were considered for the manufacture of phosphorus pentasulfide. The first involves no additional treatment. The second includes reduction of the volume of waste water discharge by the recycle of scrubber water. The third alternative includes no waste water discharge, lime treatment, alternative includes no waste water discharge, lime treatment, settling tanks, recycle of tank overflow back to the process, and landfill of sludge.

several treatment alternatives were considered for the manufacture of phosphorus trichloride and phosphorus oxychloride. The first alternative is no treatment. The second involves reduction of waste water volume by recycle of scrubber water. The third alternative includes lime treatment, settling tanks, and landfilling of sludge. The fourth alternative involves no discharge of process waste water pollutants to navigable waters.

TREATMENT OF WASTE WATERS IN THE PHOSPHATE SUBCATEGORY

Treatment of Specific Wastes

Sodium Tripolyphosphate Manufacture

suddested to brecede wet scrubbers.

As stated in Section V, two notable plants (042 and 119) achieve no discharge of process waste waters. Airborne solids collected in dust collectors from the spray dryer gaseous effluent stream are added to the product. Scrubber water is used to form a slurry with caustic in the initial neutralization step.

The manufacture of sodium tripolyphosphate is therefore a water consuming process, requiring no waste water treatment.

Calcium Phosphates Manufacture

The amount of airborne solid wastes removed by wet scrubbers can be minimized by preceding wet scrubbers with dry dust collection equipment. Treatment of phosphoric acid, suspended solids, and sludges resulting from wet scrubbing has been previously described for the phosphorus production subcategory.

Wet phosphoric acid is frequently used for animal feed grade phosphates. Fluosilicic, hydrofluoric and silicic acid wastes will subsequently result from acid defluorination. Treatment of these parameters has also been discussed previously for the phosphorus production subcategory.

Treatment Alternatives

The only treatment alternative considered for the manufacture of sodium tripolyphosphate is no discharge of process waste water pollutants.

Two treatment alternatives were considered for the manufacture of feed grade dicalcium phosphate. The first, employed by at least 50 percent of the industry, involves in-process controls for phosphate and lime dusts and phosphoric acid mists. The second alternative includes the above plus lime treatment settling, recycle of clarified water to the acid scrubbers and landfill of the sludge.

Three treatment alternatives were considered for the manufacture food grade dicalcium phosphate. No treatment is the first alternative. In the second alternative baghouses replace wet scrubbers with product recovery. Approximately 30 percent of the industry is practicing this technology. In the third alternative waste water is treated with lime, filtered, and recycled in the process. The filter cake is landfilled. Approximately 10 percent of the industry is achieving no discharge of process water pollutants by this technology.

SECTION VIII

COSTS, ENERGY AND NON-WATER QUALITY ASPECTS

INTRODUCTION

The control and treatment technologies applicable to the raw wastes of the phosphate manufacturing industry were discussed in Section VII of this report. In this Section, each of these technologies is reviewed from the following standpoints:

- * The cost of applying the technology.
- * The energy demands of the technology.
- * The impact of the technology on air quality, solid waste management, noise and radiation.
- * The recovery and subsequent use of process materials from raw waste streams, as a result of applying the technology.

A representative, hypothetical plant for each chemical produced in the industry is synthesized. Cost-effectiveness data for the plant for the various treatment alternatives (see table 17) appear as table 18. The cost is in terms of both investment cost and equivalent annual cost; and the effectiveness, in terms of pollutant quantities, is compared to the raw waste load. discussion of costs and benefits in this Section, however, is formulated to be more generally useful in evaluating the economics for any particular plant within the industry. Costs for a specific plant may be significantly influenced by the following factors which cannot all be incorporated into a single hypothetical plant:

The degree of freedom, which the personnel of each plant must retain, to choose among the alternative control and treatment technologies presented in Section VII, to choose from technologies not presented in this report, and to choose any combination or permutation of these technologies.

The cost tradeoffs, which are unique for each plant, between in-process controls and end-of-process treatments, with material recovery being an important parameter.

The real raw waste load for each plant, which may be appreciably different (in either direction) from the standard raw waste loads as presented in Section V. In particular, much greater plant-to-plant variability was observed with respect to production-normalized raw waste water quantities than with respect to production-ion-normalized raw quantities of polluting constituents.

TABLE 17
TREATMENT ALTERNATIVES

| Subcategory | Chemical | Alternative | Description |
|-------------------------|-------------------------------|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Phosphorus Producing | P4 (Fe2P) | α ω | Existing control complete recycle of phossy water. Evaporation of some other process water. Lime treatment and sedimentation of remaining process water prior to discharge. Piping, pumping, and controls for 100% recycle of process wastewaters. |
| Phosphorus | H, PO4 | А | No treatment. (Only wastewaters orginate from leaks, spills, etc.) |
| Consuming | | ω. | Tighten housekeeping and maintenance. Dike and dam around pumps, valves,, tanks, etc. Provide sumps and sump pumps. Treat with lime and landfill the sludge. |
| | P ₂ 0 ₅ | ₹8 | No treatment. Lime treatment, settling tank, recycle of tank overflow back to process, and landfill sludge. |
| 106 | P ₂ S ₅ | ∢ ‰∪ | No treatment. Recycle scrubber water. Lime treatment, settling tank, recycle tank overflow back to process, landfill sludge + B. |
| | PC1 ₃ | ∢ ⊞∪Ω | No treatment. Recycle scrubber water. Lime treatment, settling cank and landfill sludge + B. Evaporation + B + C. |
| | P0C1 ₃ | 4 B U D | No treatment. Recycle scrubber water. Lime treatment, settling tank, and landfill sludge + B. Exaporation + B + C. |
| Phosphate Producing | Na 5 3 3 10 | 4 | Dry dust collection already in existance at exemplary plant. May be economically justified on the basis of product recovery. |
| | СанРО4 | , 4 | In-process controls for phosphate and lime dusts and for phosphoric acid mists, including dry dust collection and scrubber water recycle to process. |
| | | æ | Lime treatment, settling pond, recycle of clarified water to acid scrubbers, and landfill sludge. + A. |
| | CaHPO4 Feed grade | ×ω | Replace wet scrubbers with baghouses. Lime treatment, filtration of slurry, recycle of filtrate, and landfill of filter cake + A. |
| | | | |

| Cost Wastewater TSS TDS Acidity F Per Units 1/Kkg Kg/Kkg Kg/Kkg Kg/Kkg Kg/Kkg Kg/Kkg | - 426,000 42 - 54 54 - 104,000 0.5 4 1.5 0.1 5.07 0 0 0 0 | | 0.67 | 1.54 0 | 0.44 3.000 1.87 0 | .17 \$000 5,000 5,000 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 - 5,000 | . 16 250 - 2.50 . 94 210 0.2 3.5 1.38 0 0 0 | 00 | - 6.700 22 • 6.300 22 1.54 0 0 | 4,200 100 * 2,100 50 2,30 1,800 0.06 |
|--------------------------------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------|------------------------|------------------------|---------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|--------------------------------------------|------------------------------------------|--------------------------------------------|
| y investment Annual \$1,000 Operating Costs | 500 228.2 | | 95 42.9 | 20 9.1 | 12.5 5.6 49.5 22.8 | 4.2 1.8 16.5 8.8 20.5 18.3 | 2.2 1.0 14.2 6.9 15.9 10.1 | | 186 91.6 | 200 135.0 |
| Chemical Treatment X Industry Using Alternative Alternative | Phosphorus Subcategory Pa Rav Waste 90 A 10 | Phosphorus Consuming Subcategory | H3PO4 Rav Waste (A) 90 | P205 Knw Waste (A) 100 | P255 Raw Waste (A) 100 B B 0 | PCI ₃ Rav Waste (A) 100 B 0 C 0 D 0 | POC1 ₃ Rav Waste (A) 100 C 0 D 0 | Phosphate Subcategory NasP3010 Raw Waste - | Kaupo, Roy Kaste 50 (Ford Grade) 8 50 | Raw Waste 60 (Mod Grade) A 10 |

. Use of dry dust collection and product recovery will cover cost of this alternative, hence, no cost; were listed.

There is a wide variation in the existing application of effluent control technology. Some plants have more equipment to install than others in order to meet the effluent limitations guidelines. In addition physical characteristics of each particular plant will affect treatment costs such as:

- * Plant age, size, and degree of automation.
- * Plant layout (i.e., can in-process controls be physically installed between existing units?).
- * Plant distances and topography (i.e., what are the installation and operating costs of recycle technologies?).
- * Climatic factors (temperature and evaporation/rainfall).
- * Esthetic factors (i.e., is a settling pond locally acceptable?).
- * Land availability (primarily a factor in applying settling pond and evaporation pond technologies).

The degree to which a plant is integrated with other production departments would significantly affect the cost of applying control and treatment technologies. Can waste materials from one department be used in an adjoining department (i.e., mutual neutralization of acid and alkaline wastes)? Can common treatment facilities be built (tradeoff between economies of scale vs. reversing the principle of segregation of wastes)? Are the waste water sewers from adjoining departments readily separable? The feasibility and attractiveness of joint municipal/industrial waste water treatment, which is a highly local evaluation to be made. Increasingly, more examples of such dual treatment are being reported.

The local solid waste management situation. The sludges from applying waste water treatment technologies may be landfilled at highly different costs, depending on the local availability of disposal sites and the distances involved.

In appreciation of all of the above factors, the discussion of costs in this section is formulated to be generally useful in evaluating the economics for any particular plant within the industry.

Definition of Representative Plants

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The sizes of the representative plants were chosen so that their capacities were approximately the averages of the data presented

in table 2. Although in many cases (especially in the phosphorus consuming segment of the industry) more than one product is made at a given location, each product was addressed separately in this supplement. Cost savings due to combined treatment facilities are a distinct probability. The effect in practice would be to achieve the benefits at costs lower than those presented in this analysis.

The particular assumptions in choosing representative plants were:

- Phosphorus Manufacture--The representative plant has already no discharge of phossy water (as much of the industry has). It has, in addition, achieved a level of effluent reduction commensurate with that of plant 028 (see Tables 13 and 14), but still discharges 25,000 gallons of treated process water per ton into a receiving stream. Technology "A" of Table 17, therefore, represents effluent reduction, with respect to the raw waste load, already achieved by the representative plant, with no additional costs required. The effluent from technology process re-use, and technology "B" is the implementation of this recycle. For the representative plant, it was assumed that the return water system traversed 1,000 yards back to the head end of the plant and had a difference in It 60 feet. representative plant had no severe freezing problems.
 - 2. Phosphoric Acid Manufacture--The representative plant had no process water discharge (including phossy water), but had not yet performed a systematic and thorough program for minimizing, collecting, and treating minor phosphoric acid leaks and spills.
 - 3. Manufacture of P205, P2S5, PC13, and POC13--The representative plants for these chemicals had not yet instituted any control or treatment of acid waste waters, but have already any control or treatment of phossy water. As a conservative achieved zero discharge of phossy water. As a conservative approach for PC13 and POC13 manufacture, it was assumed that approach for pc13 and poc13 manufacture, it was not feasible solar evaporation for technology "C" in Table 17 was not feasible solar evaporation for technology "C" in Table 17 was not feasible for climatic reasons so that mechanical evaporators were necessary. It was also assumed that refrigerated condensers proved less economical than larger evaporators.

The representative plants for P205, P2S5, PC13, and POC13 are assumed not to have sufficient land for settling ponds, so that mechanically raked clarifiers are used.

4. Sodium Tripolyphosphate Manufacture--The representative plant has either of two situations: (a) Dry dust collection with return of solids and wet scrubber liquors to the process has already been installed, resulting in zero discharge of process waste waters. (b) The above controls have not been installed, but can be economically justified on the basis of product recovery.

For either of these two situations (which cover much of the industry), no additional costs (attributable to effluent reduction benefits) are required.

5. Feed Grade Dicalcium Phosphate Manufacture--For control of phosphate and lime dusts and phosphoric acid mists, the representative plant has no additional required costs (attributable to effluent reduction benefits), for the same reasons as listed above for sodium tripolyphosphate manufacture.

It is assumed, however, that the representative plant uses wetprocess phosphoric acid and that it performs defluorination of all acid used (in practice, a good fraction of received acid may already be defluorinated). It is further assumed that the representative plants have sufficient land area for on-site settling ponds.

6. Food-Grade Calcium Phosphate Manufacture--The representative plant is assumed to have wet scrubbers for dust-laden vent streams. Technology A of table 17 shows the replacement of wet scrubbers with baghouses, but the cost is justified by product recovery. It is assumed that at this representative plant the elimination of wet scrubbers reduces the waste load by 50 percent.

Current Selling Prices

Table 3 shows the current list prices of the chemicals within this industry. These data are useful as a yardstick for measuring the economic impact of achieving pollution control.

Capital Cost Basis

For these analyses, the capital investment costs have been adjusted to 1971 dollars using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). The capital recovery segment of the annual costs is based on a 5-year amortization schedule, consistent with IRS regulations concerning pollutionabatement equipment and facilities, and on an 8 percent interest rate. The resulting annual capital recovery factor (principal and interest) is 0.25046.

"Taxes and Insurance" annual cost is estimated at 5 percent of the investment cost. "Operating and Maintenance" annual cost includes labor, supervision, lab support, etc., and is estimated at 15 percent of the investment cost, exclusive of chemicals, energy and power costs (which are calculated directly for each appropriate case). Chemical costs are included in "Operating and Maintenance," but power is listed separately. The cost of lime for neutralization has been assumed at \$20 per ton, and the cost of steam for evaporation has been assumed as \$0.70 per thousand pounds (or \$0.70 per million ETU).

In-Process Controls

The cost of these controls are perhaps the most difficult to generalize, since they are almost wholly dependent on the existing equipment configuration in any particular plant.

Segregation of Waste Streams

First, a plant must be surveyed to pinpoint the sources of both process water and non-contact cooling water. At one plant, there were numerous points where process water entered a common sewer, but there were relatively few cooling water sources. It was much more economical to divert the cooling water to a new and separate collection system than to adopt the reverse strategy. The project costs for such a retrofit would be highly labor intensive, especially since the construction must proceed without unduly disrupting production schedules. Other than capital recovery and associated annual costs, the annual costs would consist of a small maintenance cost and no costs for operating labor, materials or power.

There would be no effect of this project on energy demands, since plant sewers are normally gravity flow. There would be no adverse non-water quality impacts of this project.

Recycle of Scrubber Water

The capital costs would be to provide a surge tank, a recycle pump, and associated piping. The surge tank need not be large; a 15-minute residence time should suffice. The power costs and energy use of the pump would not greatly exceed the corresponding values presently utilized to provide fresh scrubber water at comparable flow rates. In any event they are small since scrubber flow rates are small.

Dry Dust Collection

Based on data furnished by the personnel of Plant 007, the capital cost of high-temperature baghouses for this 91 kkg/day (100 tons/day) plant was \$350,000. The annual operating and maintenance costs, other than capital recovery, taxes and insurance, is estimated at 6 percent of the capital cost. A credit to the annual cost is the value of recovered material; the quantity might be estimated as 2 to 5 percent of the production rat, since baghouses recover virtually all dusts. The power requirements for the fans and shakers are small, and are usually comparable to the pump power requirements for the liquid scrubbing systems they replace. Since the recovered dusts are almost always utilized in the process, there is no adverse impact on solid waste management.

Refrigerated Condensers

The condensers are standard items, and in practice the existing condensers may be used. The refrigeration supply is standard equipment, and rather expensive in terms of capital costs. An added cost would be the insulation of existing coolant lines and of the condenser. The power requirement for the refrigeration compressor could be moderately high. There would not be impact on non-water quality aspects.

Inert-Atmosphere Casting for P2S5

This is a relatively expensive control technique, requiring major revisions not only of the casting equipment but also of the basic casting procedures. There would be some small power requirements, either for inert-gas blowers or for vacuum pumps. The annual cost of the inert gas (assuming it is not recycled) must be estimated.

Housekeeping and Containment

Like the previously-discussed project of water segregation, housekeeping and containment capital costs are labor-intensive and depend to a very large extent on the existing plant configuration. A point of reference might be taken from the experience of one 360 kkg/day (400 tons/day) plant which expended \$160,000 for isolation and containment (trenches, sewers, pipelines, sumps, catch basins, tanks, pumps, dikes and curbs). The need to attend to many small sources of leaks and spills reduces the economies of scale. The power requirements are minimal, limited to small sump pumps. No adverse non-water quality impacts arise from this control technique.

TREATMENT OF SPECIFIC WASTE CONSTITUENTS

Neutralization of Acidic Waste Waters and Precipitation of Calcium Salts

A general cost factor for neutralization is 1.3 to 5.3 cents per cu m (5 to 20 cents/1,000 gallons). However, the cost for lime is directly dependent not on the waste water quantity but on the total acidity. The data of table 8, with a lime cost of \$22/kkg (\$20/ton), can be used to calculate this cost.

Neutralization tanks are usually small, with residence time varying from 30 seconds to 30 minutes. The installed cost of these tanks may be approximated by:

Capital Cost = $$15,000 \frac{\text{GPD}}{10,000} 0.2$

(Note: 1/day = 3.785 x GPD)

The power requirements for mixing are rather nominal. Assuming subsequent sedimentation or other dewatering operations, the neutralization step alone does not have any adverse non-water quality impacts.

Treatment of Arsenic-Rich Residues

The cost of this solvent is rather nominal because the quantities of waste involved are only a very small fraction of the production volume, and because the solvent (trichloroethylene) is reused, despite the high unit cost which is more than 10 cents/cu m (40 cents/1,000 gal). There is virtually no power requirement. There is, however, a very substantial impact on solid waste management, since the residues are extremely objectionable and must be disposed of in special ways. The quantity involved is 0.05 kg of AsCl3 per kkg of product PCl3 (0.1 lb/ton).

Control and Treatment of Phossy Water

Control and treatment of phossy water is a universal practice at phosphorus-producing plants. Although several different methods were observed, every plant prevents the discharge of virtually all elemental phosphorus. This technology is therefore so widely applied that costs need not be estimated; the price has already been paid. Similarly, a discussion of energy and of non-water quality aspects would be academic.

Removal of Suspended Solids

Settling Ponds

Using a detention time of 7 days and a depth of 3 m (10 ft), the calculated overflow rate is 0.42 cu m/day/m² (10 qpd/ft²). This is equivalent to 4,200 cu m/day/hectare (435,600 gpd/acre).

2 Kd/KKd (4 ID/ COM

The capital costs for small unlined ponds, with areas from 0.4 to 2 hectares (1 to 5 acres) can be estimated as:

Capital Cost = \$50,000 x Acres - \$8,000 x (Acres) 2

(Note: Hectares = 0.405 x Acres)

Because diking is a large portion of pond costs, and because the dike length increases much more slowly than pond area, larger ponds are considerably cheaper per unit area. For large unlined ponds of 40 to 1,000 hectares (100 to 2,400 acres), the capital cost is \$2,500 to \$12,500 per hectare (\$1,000 to \$5,000 per acre).

For lined ponds, the additional installed capital cost for a 30-mil PVC liner is \$21,500 per hectare (\$8,700 per acre). By using the above overflow rate and the above pond costs per unit area, a pond cost based on waste water flow may be calculated.

Settling ponds utilize no energy. The solids do, however, collect on the bottom and must either be periodically removed (creating a solid waste disposal problem), or the filled pond may be abandoned and replaced with a new one (creating a land use problem).

Mechanically-Raked Clarifiers and Thickeners

A general cost for gravity thickening is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed cost of mechanically-raked clarifiers and thickeners with capacities of 38 to 38,000 cu m/day (0.01 to 10 MGD) can be estimated as:

Capital Cost = \$95,000 (MGD) 0.4

(Note: Cu $m/day = 3,785 \times MGD$)

Where polymeric flocculants are used, the additional cost amounts to \$4 per kg of flocculant (\$1.80/lb). The dosage rate is nominally 0.05 kg/kkg of dry sludge solids (0.1 lb/ton).

The power requirements are nominal, since the rake has a very long period of revolution. Additional nominal power requirements arise from sludge pumping and clarifier overflow pumping.

This treatment has (by definition) a solid waste impact, since its function is the removal of suspended solids. The sludge from thickeners may be 85 to 92 percent moisture. If the quantities are small, this sludge may be directly transported to landfills. Alternately, it may be dewatered on sand drying beds or mechanically (filters or centrifuges) to 60-70 percent moisture before landfilling. The quantity to be landfilled is therefore a

The Phosphate Subcategory

very strong function of the degree of dewatering after thickening.

Vacuum Filtration and Centrifugation

The costs of these two mechanical dewatering techniques are competitive. A'general cost for either is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed capital costs for either vacuum filters or centrifuges are as follows:

| Capacity, MGD | cu m/Day | <u>Installed Cost</u> |
|------------------|----------------------------|------------------------------------------|
| 0.01 0.1 1 | 38 378 3785 37850 | \$25,000 25,000 200,000 750,000 |

Polymeric flocculants are often used to condition the sludge before dewatering. These costs were discussed in the previous paragraph.

The power requirements for vacuum filtration are moderate; they include the sludge pump, the flocculant pump, the rotating conditioning tank, the vacuum filter drum drive, the sludge agitator below the filter drum, the vacuum pump, the filtrate pump and the cake conveyor belt. Centrifuges have much larger power requirements, since the sludge must be accelerated to hundreds or several thousands of G's. At high speeds, the windage losses (air friction) of centrifuges are considerable. Windage centrifuges may require 40 to 75 KW (50 to 100 HP) of Large centrifuges may require 40 to 75 KW (50 to 100 HP) of power. Auxiliary power is also required for sludge pumping, flocculant pumping, centrate pumping, the cake scraper, and the cake conveyor belt.

Vacuum filters and centrifuges have a beneficial impact on solid waste management. Rather than landfilling 12 percent sludge, these devices drastically reduce the solid waste quantity by producing a 30 to 40 per-cent cake.

Centrifuges have a moderately adverse impact with regard to noise pollution, since they run with a characteristic high speed whine that is annoying to the human ear. Vacuum filtration is also noisy.

Landfilling of Solid Wastes

The disposal costs for solid wastes are highly dependent on the hauling distance. The landfill operations alone may cost \$6 or more per kkg (or per ton) for small operations and \$2 to 4 per kkg (or per ton) for larger operations.

Several pertinent papers have recently been published on the subject of solid waste management in the chemical industry. (63,64)

Solid waste hauling and the material handling operations at landfills are energy consuming operations. Landfilling of containerized soluble solids in plastic drums or sealed envelopes is practicable but expensive. Blow-molded plastic drums, made from scrap plastic (which is currently one of the major problems in solid waste disposal), could be produced for \$11-\$22/kkg (\$10-\$20/ton) capacity at 227 kg (500 pounds) solids/drum and a rough estimate of \$2.50-\$5.00 cost/drum. A more economical method, particularly for large volumes, would be sealed plastic envelopes, 750 microns (30 mils) thick.

At \$1.10/kg (50¢/lb) of film, low density polyethylene costs about 10¢ per 0.0929 square meter (1 square foot). Using the film as trench liner in a 1.8 meters (6-foot) deep trench, 1.8 meters (6 feet) wide, the perimeter (allowing for overlap) would be approximately 7.5 meters (25 feet). At a density of 1.6 grams/cc (100 pounds/cubic foot) for the solid, costs of plastic sheet per metric ton would be \$2.00 (\$1.75/ton). With sealing, the plastic envelope cost would be approximately \$2.20/kkg (\$2/ton). With additional landfill costs of \$2.20/kkg (\$2/ton), the total landfill disposal costs would be about \$4.40/kkg (\$4/ton).

The above figures for solubles disposal using plastic containers, bags, or envelopes are only rough estimates. Also, the technology would not be suitable for harmful solids or in situations where leaching contamination is critical.

Removal of Chlorides

Demineralization and Reverse Osmosis

These treatments are costly, over 10 cents per cubic meter (40 cents per 1,000 gallons).

The installed capital costs can be calculated from:

- a. Demineralization, Cap. Cost = \$280,000 (MGD) 0.75
- b. Reverse Osmosis, Cap. Cost = \$480,000 (MGD) 0.75

Hence, the capital costs for reverse osmosis are nearly double those for demineralization.

The operating costs (not including capital recovery costs) are:

- a. Demineralization, 20 cents/1,000 gal @ 1,000 mg/l TDS
 - 40 cents/1,000 gal @ 2,000 mg/1 TDS
- b. Reverse Osmosis, 38 cents/1,000 gal @ 0.01 MGD
 - 20 cents/1,000 gal @ 0.1 MGD
 - 14 cents/1,000 gal @ 1 MGD

Neither demineralization nor reverse osmosis requires a great deal of power, and neither has significant non-water quality impact.

Solar Evaporation Ponds

The installed costs of solar evaporation ponds (on the basis of pond area) are essentially the same as the costs for settling ponds presented earlier. The pond area depends in this case on the climatic differential between evaporation and rainfall:

| Evaporation-Rainfall Differential | Pond Area | | | |
|----------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|--|--|--|
| 0.6 m/yr (2 ft/yr) 1.2 m/yr (4 ft/yr) 1.8 m/yr (6 ft/yr) | 0.060 ha/cu m/day (560 acres/MGD) 0.030 ha/cu m/day (280 acres/MGD) 0.020 ha/cu m/day (190 acres/MGD) | | | |

The power requirements and non-water quality aspects of solar evaporation ponds are the same as for settling ponds. Since the residue in this case is soluble, extra disposal precautions must be taken to prevent leaching into groundwaters.

Single-Effect and Multiple-Effect Evaporators

The installed capital and operating costs for single-effect evaporators and for a 6-effect evaporator (all stainless-steel construction) are as follows:

| Capacity, GPD | Installed C | Capital Costs 6 Effects | O & M Costs. 1 Effect | \$/1,000 gal 6 Effects |
|---------------------------------------------------|-----------------------------------------------------------|--------------------------------------------|----------------------------------------------|------------------------------|
| 10,000 50,000 100,000 250,000 500,000 | 8,000 28,000 45,000 80,000 146,000 267,000 | 177,000 373,000 665,000 1,225,000 | 5.64 5.51 5.45 5.39 5.36 5.33 | 1.30 1.22 1.18 1.14 |

(Note: Liters = 3.785 x Gallons)

The energy requirements for single-effect evaporators are 555 kg-cal per kilogram of water evaporated (1,000 Btu/lb), while the 6-effect evaporator requires 100 kg-cal per kilogram of water evaporated (180 Btu/lb). The non-water quality aspects are the same as for solar evaporation ponds.

NON-WATER QUALITY IMPACT

Air Pollution

The proposed guidelines are not expected to increase air emissions. In fact, the cited technologies should decrease air

emissions in some cases where dry air pollution equipment is suggested to precede wet scrubbers. Volatilization of hazardous substances, such as fluorine, from ponds is not expected to present a problem since addition of lime will precipitate most fluorides.

Solid Waste

solid waste disposal will be the chief non-water quality area impacted by the proposed guidelines. Neutralization of acidic waste streams with lime or limestone will increase the amounts of sludge, especially when soluble phosphates and sulfates are precipitated. Installation of dry air pollution control equipment will reduce the water content of wasted solids. In addition, return of collected solids to the process may be feasible. As stated in section VII, arsenic rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. Burial in a controlled area is the standard disposal method. Special disposal methods as mentioned previously in this section may be necessary to prevent leachate from reaching surface or ground waters. Solid waste quantities and constituents are listed in Tables 9 and 10.

Energy Requirements

The energy requirements for the proposed treatment technologies are listed in table 19. For the best practicable control technology currently available the added energy requirements are insignificant when compared to the process energy requirements. Except for the production of phosphorus, energy does not significantly enter into the product cost. For best available technology economically available, the additional energy requirements for PCl3 and POCl3 are substantial. This is due to the assumption that solar evaporation ponds may not be possible in a given locale and evaporators may be necessary.

Ground Water

Since settling and evaporation ponds are extensively used for waste water treatment in the phosphate industry, it is highly recommended that all such ponds be sealed or lined so as to prevent any leakage of contaminated process waters to ground waters.

Noise

No overall adverse affect on the level of noise is expected, although individual equipment may have excessive noise levels; e.g., pumps and centrifuges.

TABLE 19

ENERGY REQUIREMENTS
FOR RECOMMENDED GUIDELINES

| | Requirement | | Percentage Energy Increase | |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|-----------------------------------------------------------|--------------------------------------------|--|
| P ₄ | 15,400 | 7.06 | 0.05 | |
| H ₃ PO ₄ P ₂ O ₅ P ₂ S ₅ PC1 ₃ (BPCTCA) PC1 ₃ (BATEA) POC1 ₃ (BATEA) POC1 ₃ (BATEA) | 48 94 9 27 27 28 28 | 0.000025 0.0126 0.75 0.13 293 0.063 146 | 0.01 8.3 0.48 1000 0.22 520 | |
| Na ₅ P ₃ O ₁₀ Calcium Phosphate animal feed gr Calcium Phosphat food grade | ade | 0 0.16 0.053 | 0 - | |

BPCTCA - best practicable control technology currently available

BATEA - best available technology economically achievable

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1977, are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the phosphate industry, this level of technology is based on the best existing performance by notable plants of various sizes, ages and chemical processes within each of the industry's categories. In some cases where no truly notable plants were surveyed, this level of technology is based on state-of-the-art unit operations commonly employed in the chemical industry.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself. Examples of in-process control techniques which are used within the industry are:

- * manufacturing process controls
- * recycle and alternative uses of water
- * recovery and/or re-use of waste water constituents
- * dry collection of airborne solids instead of (or before) wet scrubbing.

Consideration was also given to:

- a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from that application;
- b. The size and age of equipment and facilities involved;
- c. The process employed;
- d. The engineering aspects of the application of various types of control techniques;
- e. Process changes; and

0

f. Non-water quality environmental impact (including energy requirements) .

PROCESS WASTE WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents. All values of quidelines and limitations for total dissolved solids (TDS), total suspended solids (TSS), metals and harmful pollutants and and other parameters are expressed as consecutive 30-day averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration.

On the basis of the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best practicable control technology currently available in the phosphate manufacturing industry.

The Phosphorus Production Subcategory

Phossy Water

Because of the extremely harmful nature of elemental phosphorus, it is standard practice within the industry to maintain tight control over the discharge of phossy water, as discussed in Section VII.

It is apparent from the discussion in section VII that existing practicable technology can eliminate the requirements for any discharge at the TVA plant. Lime treatment of the blowdown followed by sedimentation of the precipitated phosphates and fluorides would remove the materials necessitating a blowdown, so that this treated blowdown could be recombined with the remainder of the clarified phossy water for return to the process.

There are three examples of plants which have achieved zero discharge of phossy water: Plants 159, 028, and 181.

Hence, three plants have recognized the undesirability of elemental phosphorus in any discharge and have also recognized that no practicable treatment system can remove a sufficient amount of elemental phosphorus to permit effluent discharge of phossy water wastes. They have all solved this dilemma by evaporating sufficient phospy water rather than by discharge. One plant uses an evaporation pond, while two others exploit other process heat loads for in-process water evaporation.

In view of this clear-cut demonstration within the industry, it is recommended that the best practicable control technology currently available for phossy water wastes be no discharge of pollutants to navigable waters.

Process Waters Other Than Phossy Water

The standard techniques for treating the waste waters from calciner scrubbers and from slag quenching are lime treatment and settling ponds, which perform the following functions:

* Neutralization of acid waste waters;

* Sedimentation of much of the original suspended solids in the waste waters (silica, iron oxide, and others);

* Precipitation and sedimentation of much of the phosphates, fluorides and sulfates which were dissolved in the original waste waters;

* Dissipation of the process heat to the atmosphere during the extended residence in the settling ponds:

* Reduction in the waste water quantity as a result of net evaporation during the extended residence in the settling ponds; and

* Where phossy water is combined with these other process waters, some oxidation of the elemental phosphorus to phosphates is accomplished.

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in re-use water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final re-use water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond system. Hence, fresh make-up water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

The TVA plant at Muscle Shoals, Alabama granulates the slag by quenching with a high-velocity jet of water which is recirculated from a sump in the slag pit. In this TVA operation, the cooling water and the scrubber liquors are used for make-up in slag quenching. The granulated slag effectively neutralizes these waters and also acts to filter out the scrubbed solids, which become part of the slag pile to be sold. Nearly all of the soluble phosphate and 95 percent of the fluoride is removed by the slag, and the fluoride concentration is reduced to 30 mg/l. Hence, TVA utilizes slag treatment instead of lime treatment because the slag is finely divided. Sufficient waste water treatment is obtained by TVA to enable the plant to completely reuse this water without any discharge.

Two other phosphorus plants which utilize lime treatment and sedimentation for process water treatment are Plants 028 and 159. Tables 14 and 15 list (respectively) the effluent concentrations and quantities discharged from these plants, neither of which recycles treated waste water. There are three significant differences between these two plants:

- * Plant 028 discharges into the same waterway as the plant intake so that its discharge responsibility is the net increase in constituent quantities. Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities.
- * It is apparent from the "Intake" columns of Tables 14 and 15 that the intake of Plant 159 contains much more dissolved solids (and specifically F, PO4 and SO4) than the intake of Plant 028.
- * The waste water quantity percent of production for Plant 028 is three times that of Plant 159.

The above three differences are interrelated and affect the quantities of fluoride, phosphate and sulfate discharged by Plant 159 because the effluent concentrations are of the same magnitude as the solubilities of the corresponding calcium salts. Hence, the effluent quantities are significantly influenced by factors other than the treatment of the process waters.

The effectiveness of control and treatment techniques used by the four phosphorus plants cited are summarized in Table 13. Plants 028 and 159 achieve very high (97% to 99+%) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents.

In areas of the country where very severe and extended cold weather prevails, total recycle of process water becomes difficult for two reasons:

- The return water piping and pumping must be protected against freezing. However, technology such as buried water mains and enclosed, heated pumping stations has been amply demonstrated in the chemical industry and in water supply operations.
- 2. The settling ponds may freeze. In a total recycle system, this circumstance would prevent the required water from being supplied back to the process. If auxiliary fresh water supply were provided to uncouple the process from frequent climatic perturbations, the pond system would have to consist of sufficient holding capacity to prevent temporary overflow and would have to contain sufficient evaporative capacity to prevent long-term accumulation of water.

Recommended Effluent Limitations Guidelines Pased Upon Best Practicable Control Technology Currently Available

In view of the existence of three plants (028, 159 and 181) which have already achieved zero discharge of elemental phosphorus, in view of the existence of one plant (181) which has already achieved zero discharge of all process waters, and in view of two plants (028 and 159) that are achieving exemplary performance, it is recommended that the best practicable control technology currently available for a period of 30 consecutive days be:

Total suspended solids Total phosphorus Fluoride Elemental phosphorus pH 0.5 kg/kkg (1.0 lb/ton)
0.15 kg/kkg (0.3 lb/ton)
0.05 kg/kkg (0.10 lb/ton)
No detectable quantity
Within the range 6.0 - 9.0

Waste Water from Ore Washing or Beneficiation

The best practicable control technology currently available recommended in the previous paragraphs does not include wastes from the beneficiation or washing of phosphate rock. This beneficiation is commonly but not exclusively conducted at a separate off-site location. The huge raw waste load from beneficiation, 7.5 kkg of gangue per kkg of phosphorus eventually produced, warrants a separate study and separate effluent limitations guidelines.

The Phosphorus Consuming Subcategory

Phossy Water

Gross discharges of phossy water are presently avoided by pumping displaced phossy water from the plant's phosphorus storage tank back into the emptying rail car which brought the phosphorus, and by transporting this displaced phossy water to the phosphorus producing plant for treatment and/or re-use. Such is the practice at Plants 037 and 192.

Smaller quantities of phossy water discharge may also be eliminated through the use of standard engineering techniques. The phosphorus storage tank level control system may be altered to provide an auxiliary water overflow tank with return of the water to the main tank. The avoidance of elemental phosphorus in plant sewer lines can be implemented with more stringent process and operator controls and procedures and by providing traps downstream of reaction vessels.

In view of the harmful qualities of elemental phosphorus and in view of the available choices from state-of-the-art control techniques, the recommended best practicable control technology currently available for phossy water is no discharge of pollutants.

Phosphoric Acid Manufacture

Exemplary Plant 075 operates without the discharge of any process water. There is no fundamental or practical reason why process water should be discharged at all from any dry-process phosphoric acid plant. Minor leaks and spills may be minimized, collected and treated using control techniques generally available and demonstrated in the industry.

The recommended effluent limitations guideline of no discharge of process waste water pollutants applies generally, and with special emphasis, to elemental phosphorus (i.e., phossy water) and to arsenic residues from the purification of phosphoric acid.

Phosphorus Pentoxide Manufacture

The single raw waste constituent is phosphoric acid from water tail-gas seals. Application of two standard techniques would enable total recycle of this waste water:

- Reduction in waste water quantites by using dilute caustic or lime slurry as tail gas liquor instead of pure water, increasing the absorptive capacity for P205.
- 2. Lime treatment and sedimentation to neutralize and to remove the phosphate, permitting total recycle.

In view of the straightforward application of these two techniques, the recommended best practicable control technology currently available for phosphorus pentoxide manufacture is no discharge of process waste water pollutants to navigable waters. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste as estimated in Section V.

Phosphorus Pentasulfide Manufacture

The sole source of process waste water is the scrubber liquor for fumes from casting liquid P2S5. One control technique would be the use of inert-atmosphere casting or vacuum casting to completely eliminate the need for scrubbing. As an alternate to this approach, the application of three standard techniques would permit total recycle of scrubber water:

- Use of dilute caustic or lime slurry instead of pure water would reduce the waste water quantities by increasing the adsorptive capacity for P2O5 and SO2.
- Partial recycle of scrubber liquor from a sump would reduce the waste water quantity by decoupling the buildup of absorbed acids from the mass-transfer requirements for high scrubber flow rates.
- Lime treatment and sedimentation to neutralize and to remove phosphate, sulfite and sulfate would permit total recycle.

In view of these different practicable alternatives, the recommended best practicable control technology currently available for phosphorus pentasulfide manufacture is no discharge of process waste water pollutants to navigable waters. Since total recycle is practicable technology, this recommended effluent limitations guideline is not affected by modest inaccuracies in the standard raw waste load as estimated in Section V.

This effluent limitations guideline also applies to any arsenic-rich residues from the purification of P2S5; these solid residues may be disposed of by burial as in Plants 147 and 192.

Phosphorus Trichloride Manufacture

The acid wastes from phosphorus trichloride manufacture arise from the hydrolysis of PCl3 in scrubber water from the reactor/still from product storage tanks, from product transferring operations, and from container cleaning. The scrubber water may be collected in a sump and recycled to decrease the wasted quantity of scrubber water (while still maintaining sufficient scrubber flow rates for effective mass transfer) and to increase the concentration of waste constituents.

Lime treatment of the wasted water would neutralize the acids and would precipitate the phosphite and phosphate wastes as calcium salts. Subsequent sedimentation in a mechanically-raked clarifier, with the use of a polymeric flocculant, could effectively remove 85 percent of the suspended solids as a sludge. This sludge may then be hauled as a slurry for direct landfill or may be dewatered in sand drying beds or mechanically before landfilling. The clarified water may then be discharged, with the following recommended best practicable control technology currently available:

Total Phosphorus
Total Suspended Solids,
Arsenic
pH

0.8 kg/kkg (1.6 lb/ton)
0.7 kg/kkg (1.4 lb/ton)
0.00005 kg/kkg (0.0001 lb/ton)
6.0 to 9.0

based on the raw waste load as determined in Section V:

HCl 3 kg/kkg (6 lb/ton) H3PO3 + H3PO4 2.5 kg/kkg (5 lb/ton)

The soluble CaCl2 resulting from lime-neutralization of HCl is 4.5 kg/kkg (9 lb/ton); allowing for some small amount of unprecipitated phosphite and phosphate brings the total dissolved solids to 5 kg/kkg (10 lb/ton). The quantity of precipitated 2 CaHPO3.3H2O, Ca3 (PO4)2, or 9 CaO.3P2O5.Ca(OH)2 is dependent on the relative quantities of these compounds, but is no more than 4.5 kg/kkg (9 lb/ton). With a sedimentation efficiency of 85 percent, the total suspended solids in the effluent should be no more than 0.7 kg/kkg (1.4 lb/ton).

In the case of PCl3 manufacture, the soluble chlorides are not removed by the applicable "best practicable control technology currently available," so that the recommended best practicable control technology currently available is not zero discharge. In treating the raw wastes, the total quantity of constituents is not reduced: 5.5 kg/kkg (ll lb/ton) in the raw waste vs. 5.7 kg/kkg (ll.4 lb/ton) in the treated effluent. However, the treatment does remove the acidity, substituting for it residual alkalinity.

Zero discharge of arsenic-rich reactor/still residues is recommended, since trichloroethylene treatment (as described in Section VII) may be applied.

Phosphorus Oxychloride Manufacture

The types of raw wastes, the types of applicable control and treatment technologies, and the reason for the best practicable control technology currently available not being zero discharge, are all identically parallel for POCl3 manufacture as they are for PCl3 manufacture. The difference is one of magnitude. For POCl3 manufacture, the raw waste load as determined in Section V is:

HC1 H2PO3 + H3PO4 2 kg/kkg (4 lb/ton) 0.5 kg/kkg (1 1b/ton)

Using the same rationale as for PCl3 manufacture, the recommended best practicable control technology currently available effluent limitations guideline are:

Total Phosphorus Total Suspended Solids, 0.15 kg/kkg (0.3 lb/ton)

....

1 2

0.17 kg/kkg (0.34 lb/ton)

6.0 to 9.0

Occidental Chemical Compan

The Phosphate Subcategory

Sodium Tripolyphosphate Manufacture

Exemplary Plant 042 has no process wastes. The dust collected from the spray-dryer gaseous effluent stream is added to the spray-dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray-dryer vent line upstream of the scrubbing operation.

This plant is an excellent example where a combination of inprocess controls such as dry dust collection, water re-use, and return to the process of airborne solids have been utilized to totally avoid any aqueous wastes. Plants 006 and 119 also have no discharge of process waters.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters.

Animal-Feed Grade Calcium Phosphates

Exemplary Plant 182 has no process wastes. Three separate water cycles are used, and there is no effluent from any of them. The acid defluorination scrubber water is neutralized with lime, the solids are settled by ponding, and the pond effluent is reused as scrubber water. The scrubber water for collection of airborne solids from the reactor and dryer is recirculated with a bleed-off directly into the reactor as process water. Cooling water is recycled through a cooling tower, with the blowdown used as make-up in the solids scrubbing system instead of being wasted. Softened well water is used for cooling water make-up.

This plant is an excellent example where a combination of inprocess controls (dry dust collection, recycle of scrubber water to minimize waste water quantities, return of process waste streams to the process, and a systems approach towards water use whereby a blowdown stream from one water cycle becomes a make-up stream for another) in combination with a standard limetreatment, sedimentation and total recycle scrubber water system results in the discharge of no aqueous wastes.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters.

Food-Grade Calcium Phosphates

The raw aqueous wastes from the manufacture of food grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely divided calcium phosphate solids and phosphoric acid from acid units and from excess acid in the reaction liquid. The total raw waste load (from Section V) is:

Process Water Wasted
Total Suspended Solids (2.4%)

Phosphoric Acid (0.7%)

4,200 1/kkg (1,000 gal/ton)

100 kg/kkg (200 lb/ton)

30 kg/kkg (60 lb/ton)

The first type of currently available control technology that may be applied is the substitution of dry dust bag collectors for wet scrubbers, as has been done at Plants 003, 042, 119, and 182. The fact that a multi-product plant must provide a separate baghouse for each product does not deny the current availability of this technology, but rather increases the cost of such an installation. However, Plant 003, which is a multiple-product, food grade, calcium phosphates plant, has justified the installation of separate baghouses on the sole basis of profitability from product recovery.

The elimination of wet scrubbing systems would halve the aqueous waste load so that it would then consist of 2,100 1/kkg (500 gal/ton), containing 2.4 percent of suspended solids amounting to 50 kg/kkg (100 lb/ton) and containing 0.7 percent of phosphoric acid amounting to 15 kg/kkg (30 lb/ton).

Lime treatment, clarification and sedimentation (with the aid of polymeric flocculant) may then be used to precipitate the phosphate and remove suspended solids to 25 mg/l. The clarifier underflow will remove the bulk of the suspended solids. Dewatering of these solids may be required to make them suitable for landfill. The practice at Plant 006 after lime treatment for neutralization and precipitation of phosphate wastes is vacuum filtration of the slurry from the clarifier underflow. The water lost with the solids reduces the effluent flow to 1800 l/kkg (430 gal/ton) containing:

Suspended Solids 0.06 kg/kkg (0.12 lb/ton)
Total Phosphorus 0.03 kg/kkg (0.06 lb/ton)

SUMMARY OF PROPOSED BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

No Discharge of Process Waste Water Pollutants

The proposed best practicable control technology currently available for process waste water is no discharge of pollutants for the manufacture of the following chemicals:

Phosphorus Consuming Subcategory
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphate Subcategory
Sodium Tripolyphosphate
Calcium Phosphates (Animal-Feed Grade)

Permitted Discharge

The proposed best practicable control technology currently available for process water for the manufacture of phosphorus (and ferrophosphorus). PCl3, POCl3 and food grade calcium phosphate require that the average of daily values for 30 consecutive days shall not exceed:

| | Phosphorus and <u>Ferrophosphorus</u> | Phosphorus Trichloride | Phosphorus <u>Oxychloride</u> | Food Grade Calcium Phosphate |
|------------------------------------------|---------------------------------------------|---------------------------|----------------------------------|------------------------------------|
| Suspended Solids kq/kkg Total Phosphorus | 0.5 | 0.7 | 0.15 | 0.06 |
| kg/kkg Fluoride | 0.15 | 0.8 | 0.17 | 0.03 |
| kg/kkg | 0.05 | | | |
| Arsenic kg/kkg | | 0.00005 | | |
| Hq | 6.0-9.0 | 6.0-9.0 | 6.0-9.0 | 6.0-9.0 |

The above guidelines apply to maximum averages of daily values for any period of 30 consecutive days.

The pH range is to be maintained at all times.

The permitted maximum concentration for any one day period for suspended and dissolved solids is twice that of the consecutive 30 day average value.

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1983, are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the phosphate manufacturing industry, this level of technology was based on the very best control and treatment technology employed by a specific point source within the category or subcategory, or where it is readily industrial another. from one industry process to transferable achievable places equal economically available technology emphasis on in-process controls as well as on control or treatment techniques employed at the end of a production process.

Those plant processes and control technologies which at the pilot plant, semi-works, or other level have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing the best available technology economically This technology is the highest degree of control achievable. technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and Although "no discharge" of pollutants. factors are considered in this development, the costs for this level of control are intended to be for the top of the line of current technology subject to limitations imposed by economic and engineering feasibility. However, best available technology economically achievable may be characterized by some technical risk with respect to performance and with respect to certainty of technology may necessitate some this Therefore, costs. industrially sponsored development work before its application.

The following factors were taken into consideration in determining the best available technology economically achievable:

- a. The age of equipment and facilities involved;
- b. The process employed;
- c. The engineering aspects of the application of various types of control techniques;
- d. Process changes;
- e. Cost of achieving the effluent reduction resulting from application of best available technology economically achievable; and

51. Joint Hearings on the National Environmental Policy Act

f. Non-water quality environmental impact (including energy requirements).

PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents.

On the basis of the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of the phosphate manufacturing industry.

All Chemicals Except Phosphorus, Phosphorus Trichloride, Phosphorus Oxychloride and Food Grade Calcium Phosphate

The recommended best available technology economically achievable for process water are the same as the best practicable control technology currently available effluent limitations guidelines, technology currently available effluent pollutants to navigable i.e., no discharge of process waste water pollutants to navigable water for the manufacture of the following chemicals:

Phosphorus-Consuming Subcategory
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphate Subcategory
Sodium Tripolyphosphate
Calcium Phosphates (Animal Feed Grade)

The Phosphorus Production Subcategory

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in re-use water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final re-use water supply ponds, thereby minimizing the quantitites of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond evaporation in the process and to net evaporation in the system. Hence, fresh make-up water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

It is therefore recommended that the best available control technology economically achievable for phosphorous production be no discharge of process waste water pollutants to navigable waters.

Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride

In-Process Controls

The largest contribution to the raw waste load from these processes is from the escape of PCl3 vapor from the reactor/stills. The methods for drastically reducing this contribution are clear cut: the substitution of refrigerated condensers for water-cooled condensers or the addition of refrigerated condensers downstream of water-cooled condensers. Refrigerated condensers are already in use at Plant 037 in the manufacture of POCl3 by the air-oxidation process.

As an added step, a demister can be added downstream of the refrigerated condenser to prevent condensed but dispersed PCl3 from escaping to the scrubber. One concept for this demister is a short section of column packed with metal packing (for good heat transfer) within the refrigerated condenser.

As a corollary to this principle, other sources of PCl3 and POCl3 vapors could be controlled by refrigerated condensers or cold traps. The storage tank vent and vents for the transfer of liquid products are included in this concept. Alternatively, the liquid products could be maintained at low temperatures by refrigerating coils in the storage tanks so that vapors from storage and transfer would be minimized.

In view of the order-of-magnitude or greater reduction in the vapor pressure of these products resulting from readily available refrigeration levels, plus the effect on PCl3 condensation from doubling (or more) the temperature driving force for heat transfer, a reasonable expectation is that the PCl3 vapor (and mist) losses could be cut to 10 percent of the present values.

The acid wastes from washing tank cars and tank trucks, and from washing used POCl3 filter elements are very small at present, amounting to 0.014 kg/kkg (0.028 lb/ton) of HCl and 0.003 kg/kkg (0.007 lb/ton) of total phosphates (see table 8). These are very small fractions of the total raw waste load discussed in section v. The wastes from washing returnable nickel drums, however, is estimated to be much larger. Should this raw waste indeed prove significant, the returnable container use could be abandoned in favor of non-returnable, epoxy-lined drums (as is the partial practice at Plant 147 for PCl3).

Another minor source of waste water is the generation of HCl (not PCl3) from the reactor/stills, resulting from small quantities of stray moisture in the vessels. The HCl is driven off as a non-

condensible while the corresponding H3PO3 and H3PO4 is retained as reactor residue.

All in all, the above outlined in-process control techniques could drastically reduce the raw waste load to perhaps 10 percent of the original value, so that the estimated raw waste quantities would then become (for either PCl3 or POCl3 manufacture):

HCl 0.3 kg/kkg (0.6 lb/ton) H3PO3 + H3PO4 0.25 kg/kkg (0.5 lb/ton)

As important as the reduction in the waste water constituent quantities would be a corresponding reduction in the quantity of waste water generated. Tail-gas scrubbers should be very smaller and should require much lower water flow rates.

As an added step, the scrubber water could be recycled from a sump, thereby decoupling the waste water quantity (blowdown from the sump) from the mass-transfer requirements for scrubbing furthermore, water use could be cascaded in the plant; for example, the waste water from tank car washing could be used as make-up in the tail-gas scrubber system.

End-of-Process Treatment

At the new low levels of waste water flow rates and constituent quantities, simple lime neutralization of moderate pH (without sedimentation) would result in the following waste water characteristics:

Waste water Quantity
Total Dissolved Solids
Total Suspended Solids
pH

500 1/kkg (120 gal/ton)
0.5 kg/kkg (1.0 lb/ton)
0.35 kg/kkg (0.7 lb/ton)
6-9

Further lime neutralization and removal of suspended solids would not appreciably reduce the quantity of total dissolved solids, and would trade off reduction in total suspended solids for higher pH levels.

At this point, the waste water quantity would be extremely low, and a practicable final step would be evaporation to dryness. An idea of the costs of evaporation can be obtained by assuming a plant manufacturing 59 kkg/day (65 tons/day) of total PCl3 and POCl3. The waste water quantity would be 30,000 liters/day POCl3. Using the data of Section VIII for single-effect evaporation,

Capital Cost = \$6,700
Annual Costs: Capital Recovery = \$1,600
Taxes & Insurance = 300
Operation & Maintenance = 14,700
(including energy) \$16,600

Unit | Cost = \$0.85/kkg (\$0.77/ton)

This unit cost is only 0.3 percent of the current selling price, \$295/kkg (\$268/ton).

It is entirely possible that a rigorous economic evaluation might result in a decision to dispose of the original raw waste load by evaporation, rather than to bear the expense of the in-process controls discussed above which minimize (but do not eliminate) the waste. The waste water quantity to be evaporated would be the original quantity, 5,000 l/kkg (1,200 gal/ton), or 300,000 liters/day (78,000 gal/ton); and the costs would be:

Capital Cost = \$38,400
Annual Costs: Capital Recovery = 8,900
Taxes & Insurance = 1,900
Operation & Maintenance = 147,000
(including energy)
Unit Cost = \$8.10/kkg (\$7.35/ton)

The most conservative approach, i.e., to evaporate all of the waste water without any in-process control to reduce its quantity, would cost 2.8 percent of the current selling price. The fundamental reason is that despite the high unit cost of evaporating water, the waste water quantities for PCl3 and POCl3 are very small. The conclusion is reached that the application of this available technology is economically achievable.

The final step of total evaporation would bring the PCl3 and POCl3 manufacturing processes into line with the rest of the phosphate industry by achieving the national goal of eliminating the discharge of all pollutants.

It is therefore recommended that the best control technology economically achievable for PCl3 and POCl3 manufacture be no discharge of process waste water pollutants to navigable waters.

Food Grade Calcium Phosphate Manufacture

After elimination of wet scrubbers as described in Chapter IX standard lime treatment and sedimentation may be used to neutralize these remaining wastes, to precipitate the phosphate, and to remove a nominal 85 percent of the suspended solids (with the possible aid of a polymeric flocculant). At a pH of 10.5, the remaining concentration of dissolved solids would be approximately 0.3 mg/l. The quantity of waste water would be approximately 85 percent of concentration of dissolved solids with the remainder landfilled with the underflow from the clarifier as wet sludge. The clarified overflow would than consist of 1,800 l/kkg (430 gal/ton) containing:

Dissolved Solids 0.0005 kg/kkg (0.001 lb/ton) Suspended Solids 11 kg/kkg (22 lb/ton)

The demonstrated practice at Plant 006, after lime treatment for neutralization and for precipitation of phosphate wastes, is vacuum filtration of all of the slurry from the clarifier underflow.

Vacuum filtration (possibly after conditioning with a polymeric flocculant) can reduce the suspended solids content of the waste water from phosphates to the level of 0.5 mg/l. Based on these data and on the level of dissolved phosphates of 0.3 mg/l, the discharge would contain on the basis of the total process water wasted, 4,200 l/kkg (1,000 gal/ton):

Total Dissolved Solids 0.0015 kg/kkg (0.003 lb/ton)
Total Suspended Solids 0.0025 kg/kkg (0.005 lb/ton)

With the achievement of these extremely low levels of TDS and TSS, or even with considerable relaxation of these levels, the treated-waste water from the manufacture of food grade calcium meet the U.S. Food and Drug expected to phosphate is Administration criteria for process water and this treated water can then be recycled back into the process. No product purity restrictions exist any longer which had previously necessitated discharge. In fact, once the commitment to total recycle is made, the lime treatment step may be bypassed since the ionic species from the dissolved solids and the phosphoric acid are precisely those desired in the reaction vessel. However, the problem of waste segregation is sufficiently great that for reasons of product purity existing plants may not be able to make the necessary changes by 1977.

It is therefore recommended that the best available control technology economically achievable for food grade calcium phosphate manufacture be no discharge of process waste water pollutants to navigable waters.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT RECOMMENDATIONS

INTRODUCTION

This level of technology is to be achieved by new sources. term "new source" is defined in the Act to mean "any source, construction of which is commenced after publication of proposed regulations prescribing a standard of performance." New source performance standards are to be evaluated by adding to the consideration underlying the identification of best available technology economically achievable a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process technology identified in best available technology control economically achievable, new source performance standards are to be based on an analysis of how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods and other alternatives were to be However, the end result of the analysis identifies considered. standards which would reflect levels of control effluent achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination which was to be made for new source performance standards is whether a standard permitting no discharge of pollutants is practicable.

The following factors were considered with respect to production processes which were analyzed in assessing new source performance standards:

- a. The type of process employed and process changes;
- b. Operating methods;
- c. Batch as opposed to continuous operations;
- d. Use of alternative raw materials and mixes of raw materials;
- e. Use of dry rather than wet processes (including substitution of recoverable solvents for water); and
- f. Recovery of pollutants as by-products.

PROCESS WATER GUIDELINES

On the basis of the information contained in Sections III through X of this report the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various categories of the phosphate manufacturing industry.

Since the best practicable control technology currently available effluent limitations guidelines for all of the chemicals considered in this study of the phosphate category were no discharge of process waste water pollutants to navigable waters, the recommended new source performance standards are identical to the best available technology economically achievable.

PRETREATMENT RECOMMENDATIONS

In addition to the recommendation of new source performance standards and related effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter waste water treatment plant were identified. A determination was made of whether the introduction of such pollutants into the treatment plant should be completely prohibited.

Waste Water Flow Rate

A determination must be made on an individual basis about the impact of a plant's discharge on the total hydraulic capacity of both the municipal collection system and the municipal waste water treatment plant. At an extreme, hydraulic overloading will result in overflows or by-passes as the capacities of pumping stations (both in the collection system and the raw waste water pumping stations at the treatment plant) are exceeded. It must be remembered that an overflow of combined industrial/municipal waste water has the same adverse environmental effect as an overflow of raw domestic sewage. At a minimum, hydraulic overloading would result in reduced efficiency of the treatment plant because:

- * Primary and secondary clarifiers would be operating at excessive overflow rates;
- * Secondary treatment units (activated sludge or trickling filters) would be operating at a food deficiency since the waste water from the phosphorus chemicals industry would provide no organic material;
- * Trickling filters would become flooded (and so anaerobic);
- * Grit chambers would have a high linear velocity resulting in the carry-over of grit and the subsequent adverse effects on equipment;
- * The capacity of air blowers for activated sludge secondary treatment may be exceeded, resulting in reduced

levels of dissolved oxygen;

* The capacity of chlorinators may be exceeded, resulting in insufficient disinfection; and

* The critical operating parameters of the activated sludge unit may be compromised.

The domestic waste water flow rate follows a well-known diurnal cycle; if the industrial contribution could be staggered to provide flow equalization, the impact of the added flow rate could be minimized. Conversely, sporadic slug discharges could make periodic overloading more probable.

Suspended Inorganic Solids

High concentrations of suspended inorganic solids might overload the primary sludge collectors, the primary sludge pumps, the sludge thickener, the sludge dewatering operation, and the sludge disposal system. In addition, since these solids provide no organic food for secondary treatment organisms, they would reduce the active biological-solids fraction (i.e., reduce the mixed liquor volatile suspended solids), thereby reducing the efficiency of secondary treatment.

Acidity

While moderate alkalinity may be tolerated since carbon dioxide produced in secondary treatment by the microbial oxidation of organic material will provide neutralization, free mineral acidity normally cannot be tolerated by the organisms in the secondary treatment biomass. The proteins in these organisms are precipitated and coagulated at pH 4 to 5.

Another strong reason for avoiding acidic contributions to publicly-owned treatment plants is that acidic wastes would drastically promote corrosion of equipment.

It is recommended that the allowable pH range be set at 6 to 10.5.

Dissolved Inorganic Solids

Dissolved inorganic solids would pass through a secondary waste water treatment plant without being removed. Hence, reliance on publicly owned treatment plants would be no treatment at all with respect to dissolved solids, and it would be equivalent to direct discharge.

The pretreatment standards for dissolved inorganic solids should be the same as the applicable or proposed effluent limitations guidelines.

Heavy Metals or Harmful Materials

Metals or harmful materials would at best, pass through a publicly owned treatment plant, and at worst, adversely affect the microorganisms in secondary treatment. Elemental phosphorus (as phossy water) and enriched arsenic compounds are substances that may be discharged into municipal sewer systems from this industry. Special attention is brought to pretreat wastes for removal of these materials.

It is recommended that the pretreatment standards be no discharge of metals or harmful materials.

Dissolved Phosphates

While dissolved phosphates would generally pass through secondary treatment plants with the waste water treatment plant effluent, they would affect the sludge operations. Gravity-thickened sludge (6 to 12 percent solids) is normally conditioned with lime, ferric chloride, or alum before dewatering operations, although polymeric flocculants are also widely used. The phosphates would be precipitated as the calcium, ferric, or aluminum phosphate and would thus render the conditioning step ineffective by partially or totally removing the active cation from solution.

A similar situation exists in tertiary treatment, in the phosphate removal step using lime, ferric chloride, or alum. In this case, the chemical requirements would be increased and the sludge handling capacity of the treatment plant could be overloaded. While these pretreatment standards apply only to secondary plants, precautions should be taken to avoid adverse effects when tertiary treatment might be added in future years.

Summary of Recommended Pretreatment

Due to the nature of the process waste waters of the phsophorus producing and the phosphorus consuming subcategories it is recommended that these wastes not be discharged into publicly owned treatment works. These waste waters are considered to be incompatible with such works principally because of harmful constituents such as elemental phosphorus and the possible presence of arsenic, cadmium, uranium and like metals also present in the phsohate ore.

The principal contaminant from the phosphate subcategory is phosphate, which is incompatible with secondary treatment plants. However, these wastes are considered to be compatible with tertiary treatment plants designed, constructed and operated to remove dissolved phosphates.

SECTION XII

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SECTION XIV

GLOSSARY

All underlined numbers within a chemical formula represent normally subscripted numbers. Physical limitations of the printing device make this system necessary. For Example, H20 represents water.

Barn

A room-like condensation chamber for anhydrous phosphorus pentoxide.

Burden

The combined rock, coke and silica feed to a phosphorus electric furnace.

Calcination

Heating of a solid to a temperature below its melting point to bring about a state of thermal decomposition or a phase transition other than melting. (73)

DCP

Dicalcium Phosphate Dihydrate, CaHP042H20.

Dry Process Phosphoric Acid

Phosphoric acid made from elemental phosphorus. Also called furnace acid.

Eutectic

The lowest or highest melting point of an alloy or solution of two or more substances that is comprised of the same components. (73)

Ferrophos phorus_

A by-product iron-phosphorus alloy of phosphorus smelting, typically containing 59 percent iron and 22 percent phosphorus. Symbolized as Fe2P in this report.

Flux

A substance that promotes the fusing of minerals or metals or prevents the formation of oxides. For example, metal refining lime is added to the furnace charge to absorb mineral impurities in the metal. A slag is formed which floats on the bath and is run off. (73)

1797

Furnace Acid

Phosphoric acid made from elemental phosphorus. Also called dry process phosphoric acid.

Ganque

The minerals and rock mined with a metallic ore but valueless in themselves or used only as a by-product. (73)

Hydrolysis

A chemical reaction in which water reacts with another substance to form one or more new substances. (73)

Immiscible

The property of one liquid being unable to mix or blend uniformly with another.

1

liter.

MCP

Monocalcium Phosphate Monohydrate, Ca (H2PO4) 2 - H20.

Nodule

Semi-fused agglomerated and calcined phosphate rock particle.

Pdt

Product.

Phosphorus Mud

Sludge or emulsion of phosphorus, dust and water.

Phosphorus Oxychloride

POC13.

Phosphorus Pentasulfide

P2S5.

Phosphorus Pentoxide

P205.

1798

Phosphorus Trichloride

PC13.

Phossy Water

Water containing colloidal phosphorus.

Process Water

Any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate product, by-product, waste product or finished product.

Slag

The fused agglomerate which separates in metal smelting and floats on the surface of the molten metal. Formed by combination of flux with gangue of ore, ash of fuel, and perhaps furnace lining. The slag is often the medium by means of which impurities may be separated from metal. (73).

STP

Sodium Tripolyphosphate, Na5P301(.

TCP

Tricalcium Phosphate, Ca3 (PO4) 2.

Transport Water

- (1) Water used to carry solids from a site in a slurry form.
- (2) Water accompanying a chemical in transport which is either immiscible with water or highly insoluble in water. The water acts as a blanket preventing contact of air or other substances with the chemical.

Wet Process Phosphoric Acid

Phosphoric acid made from phosphate rock and sulfuric acid.

TABLE 20

MUTRIC UNITS

CONVERSION TABLE

| MULTIPLY (ENGLISH | UNITS) | by | TO OBTAIN (| METRIC UNITS) |
|-------------------------------|--------------|---------------|--------------|--------------------------------|
| ENGLISH UNIT | ABBREVIATION | CONVERSION | ABBREVIATION | METRIC UNIT |
| acre | ac | 0.405 | ha | hectares |
| ecre - feet | ac ft | 1233.5 | cu m | cubic meters |
| British Thermal | | | | |
| Unit | BTU | 0.252 | kg cal | kilogram-calories |
| British Thermal Unit/pound | ETU/1b | 0.555 | kg cal/kg | kilogram calories/ kilogram |
| cobic feet/minute | cfm | 0.028 | cu m/min | cubic meters/minute |
| cubic feet/second | cfs | 1.7 | cu m/min | cubic meters/minute |
| cubic feet | cu ft | 0.028 | cu m | cubic meters |
| aubic feet | cu ft | 28.32 | 1 | liters |
| cubic inches | cu in | 16.39 | cu cm | cubic centimeters |
| degree Fahrenheit | • F | 0.555(°F-3 | 2) * °C | degree Centigrade |
| feet | ft | 0.3048 | מ | meters |
| gallen | ga1 | 3.785 | 1 | liters |
| gallon/minute | gpm | 0.0631 | 1/sec | liters/second |
| horsepower | hp | 0.7457 | kw | killowatts |
| inches | in | 2.54 | cm | centimeters |
| inches of mercury | in Hg | 0.03342 | atm | atmospheres |
| pounds | 16 | 0.454 | kg | kilograms |
| nillion gallons/da | ay mgd | 3,785 | cu m/day | cubic meters/day |
| mile | mi | 1.609 | kn | kilometer |
| pound/square inch (gauge) | psig | (0.06805 psig | ; +1)*atm | atmospheres (absolute) |
| square feet | sq ft | 0.0929 | sq m | square meters |
| square inches | sq in | 6.452 | sq cm | square centimeters |
| ters (short) | ton | 0.907 | kkg | metric tons |
| | | | | (1000 kilograms) |
| yard | yd | 0.9144 | m - | meters |

^{*} Actual conversion, not a multiplier

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HOOKER CHEMICALS & PLASTICS CORP., ET AL.,

Petitioners,

v.

No. 74-1687

RUSSELL E. TRAIN,

Respondent.

CERTIFICATE OF SERVICE

I hereby certify that on this 20th day of December, 1974, one copy of the Deferred Joint Appendix to the briefs in the above-captioned cases was served on counsel for Respondent by placing same in the United States mail, first class, postage prepaid, properly addressed to John J. Zimmerman, Attorney, Department of Justice, Washington, D.C.

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